WATER AND ION FLOW THROUGH IMPERFECT OSMOTIC MEMBRANES

By

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INTRODUCTION

As the population of the world continues to increase, greater and greater demands are being made upon the available fresh water resources. Consequently, there are many heavily populated regions of the world in which fresh water is becoming increasingly scarce. The problem is especially acute in southwestern United States and in the Mediterranean area. Fresh water needs could be more than adequately met if an economical process could be found for purifying saline waters. In order to develop a suitable process, the Congress of the United States has set up the Office of Saline Water under the Department of the Interior. This Office is considering every conceivable means for removing salt from saline waters. One promising method is based upon the principle of osmosis. At the University of Florida, the Department of the Interior is supporting a program to explore this particular method for purifying sea water.

The phenomenon of osmosis has long been of scientific interest. As far back as the eighteenth century it was observed that when certain aqueous solutions were separated from water by animal membranes, water spontaneously passed through the membrane into the solution. The membrane

served the function of permitting the water to pass while blocking the counter-flow of the solute. J. H. van't Hoff (1) described these membranes as semipermeable.

Since then, osmosis has had a significant place in textbooks on physical chemistry. It is frequently used to illustrate the concept of reversibility. Consider an osmotic cell in which the water is passing from the fresh water side through a semipermeable membrane into an aqueous salt solution. This flow of water through the membrane can be retarded by applying pressure to the solution. The pressure at which flow stops is the osmotic pressure. If the pressure is decreased by an incremental amount, water will again begin flowing into the solution. But if the pressure is increased by an incremental amount, a reverse flow of water will occur from the salt solution to the pure water side. The term reversible is used to describe this process.

Recently it has been suggested (2) that this effect of reverse osmosis might be practical for purifying saline waters. Since the process would approximate reversible conditions, the energy requirements should approach the thermodynamic minimum required to separate salt from sea water.

However, no membrane was known that could be used in such a process. In fact, no synthetic organic membrane had yet been discovered that would function effectively as

a semipermeable membrane in salt water.

This, then, is the problem with which this dissertation is concerned--the semipermeability of synthetic organic membranes in strong electrolytes.

In Chapter I the discovery of a membrane (cellulose acetate) which is semipermeable in strong electrolytes is described. This discovery prompted much curiosity about the mechanisms involved in the transfer of water and ions across the membrane. A theory of these mechanisms is proposed in Chapter II. In the two subsequent chapters, various tests of the theory are described.

Although the discovery of cellulose acetate as an effective semipermeable membrane was a big step in the development of an osmotic membrane for the purification of saline water, yet for various reasons this membrane would not be practical. One of the reasons is its limited life. After several weeks of continuous use, cellulose acetate ceases to behave as a semipermeable membrane in strong electrolytes. In order to extend the life of the membrane it is necessary to gain an understanding of the process involved in film failure. This work is presented in Chapter V.

In order to maintain continuity throughout the text of the dissertation, experimental details have been placed in the Appendix.

CHAPTER I

DISCOVERY

Review of the Literature

Most of the studies on osmosis reported in the literature have dealt with systems in which the solutes were relatively large organic molecules. Usually cellophane, collodion, and natural membranes were used. Very little has been reported on osmosis of solutions of strong electrolytes. This is due mainly to the difficulty which has been encountered in finding a semipermeable membrane for these systems.

Certain biological membranes are known to function as osmotic membranes in strong electrolytes. Cooper (3), for example, has reported that the membrane in a particular species of seaweed found off the coast of India is semipermeable in sea water.

Of all the reported attempts to synthesize a perfect osmotic membrane, the copper ferrocyanide membrane, first discovered by M. Traube in 1864, comes closest to achieving this goal. Using this membrane, Morse (4) perfected a technique for measuring high osmotic pressures. Employing a 0.5 N potassium chloride solution, this membrane was able

to hold an osmotic pressure of twenty atmospheres for twenty days. However, the film failed rapidly in succeeding experiments. Berkeley and Hartley (5), employing the same membrane, measured the osmotic pressure of a wide range of inorganic electrolytes. More recent work with this film has been reported by Craig (6) and Mibashan (7).

The literature survey revealed that several synthetic organic membranes have been evaluated. Trautmann and Ambard (8) have checked the semipermeability of cellophane in solutions of uni-univalent and uni-bivalent salts. When a 0.0017 molar solution was forced through cellophane, they found that it prevented the passage of 30 per cent of the uni-univalent salts and 75 per cent of the uni-bivalent salts. Baumgarth (9) checked the effect of ultrasonics on the diffusion of NaCl through cellophane and observed that its rate of diffusion was increased.

Dried collodion membranes have been found by Northrop (10) to be only slightly permeable to salts of strong acids and bases, yet highly permeable to water. Employing various special treatments, Sollner (11), Elford (12), and others have also worked with collodion membranes.

Burgess (13) made osmotic films from sodium alginate that retarded the passage of the sodium ion.

An apparatus for ultrafiltration has been described by Baudouin and Lewin (14) in which a cellulose acetate

membrane was used. However, no mention was made in the abstract of filtering solutions of strong electrolytes. Recently Terazawa (15) has proposed that in general crystalline semipermeable membranes should be impermeable to ions of strong electrolytes. He classified copper ferrocyanide as a crystalline membrane. Gels are another type of film that may function as osmotic membranes. In this category Hermans (16) has evaluated the osmotic properties of cellulose xanthate gels in strong electrolytes.

Semipermeability Tests

In order to find a semipermeable membrane for strong electrolytes, a trial-and-error approach was used--although it was felt that the desired membrane should contain some hydrophilic groups. Many types of thin films were obtained from the leading chemical manufacturers in the country. Some films were prepared in the laboratory. The apparatus that was ultimately developed for measuring the semipermeability is shown in Figure 1. It embodied the following features: (1) Pressures up to 2000 p.s.i. could be obtained by means of compressed air or nitrogen. (2) Stirring was accomplished by convection. One leg was heated and the other cooled. (3) Monel was used throughout, which reduced corrosion to a minimum. (4) The membrane was supported by a ceramic disc which was recessed into the base

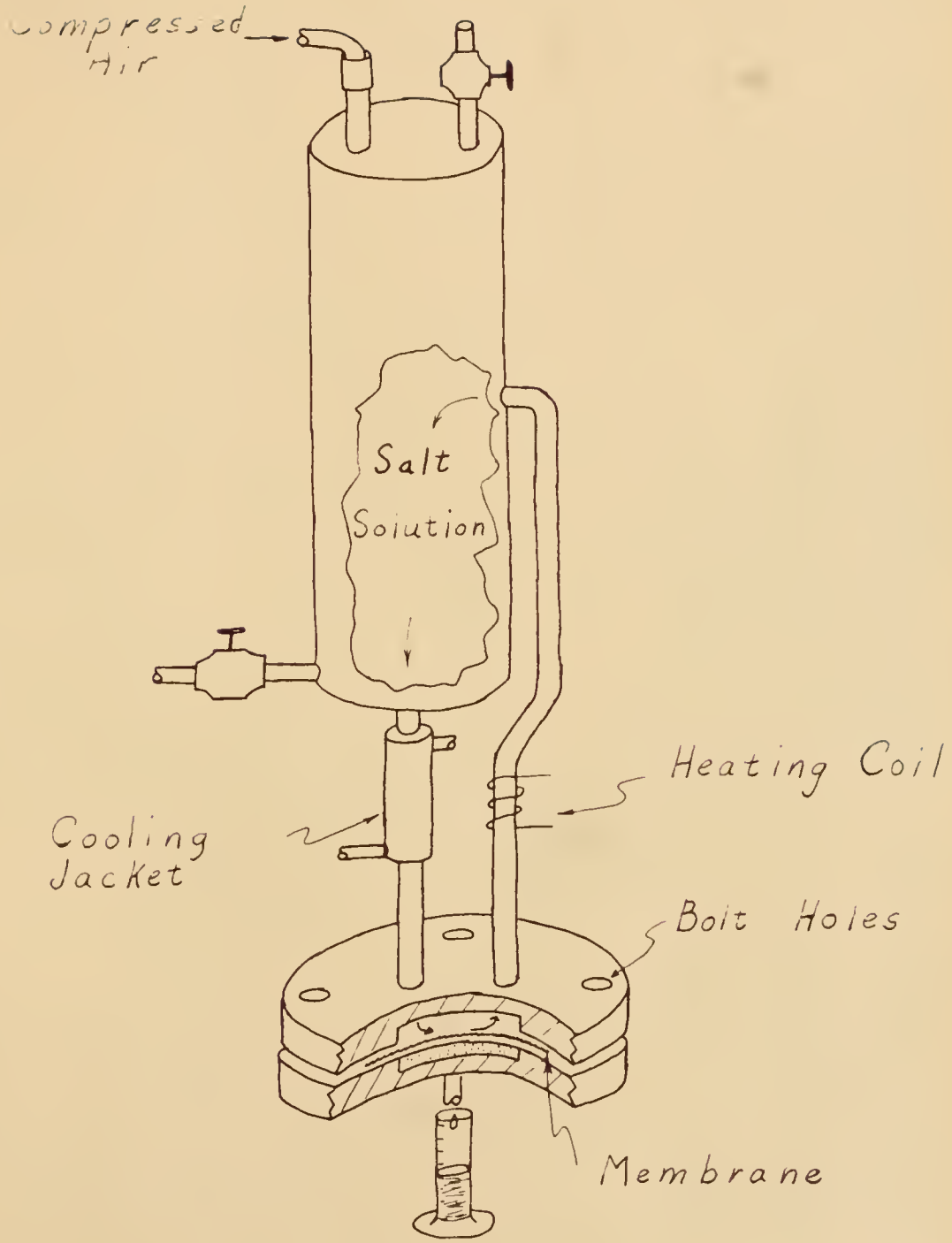

Fig. 1.--Apparatus for determining the semi-permeability of imperfect osmotic membranes.

plate and turned on a lathe to a flat surface. This design permitted the testing of very thin films at high pressures.

To measure the semipermeability, a film was first clamped into place as illustrated in Figure 1. The apparatus was filled with salt solution and the pressure applied. Water that passed through the membrane was collected at the bottom and analyzed. From the concentration of salt in the apparatus and that in the water that had passed through the membrane, the percentage of salt rejected was calculated. The percentage of salt rejected is taken as a measure of semipermeability.

The results of the screening program are recorded in Table 1. As can be seen by the table, the semipermeability of du Pont cellulose acetate far exceeded that of any other film tested. Consequently, further study was confined for the most part to cellulose acetate membranes. The semipermeability of du Pont CA-48 cellulose acetate to various solutions is given in Table 2.

These results were significant. They indicated that it is possible to synthesize an organic membrane that is semipermeable in strong electrolytes. However, the cellulose acetate membranes that were tested could not be used as ultrafilters for purifying saline waters--first, because the rate of filtration would be too slow and second, because their life was limited to only a few weeks.

TABLE 1

SEMIPERMEABILITY OF VARIOUS MEMBRANES TO AQUEOUS SODIUM CHLORIDE SOLUTIONS

Membrane Tested	Pressure on Membrane p.s.i.	Semipermeability, % Rejection[a] of Dissolved NaCl by Membrane	Remarks
Polyvinyl alcohol (du Pont Elvanol 71-24)	100	None	Effluent pH - 11
Polyvinyl alcohol (Baked at 145°C.)	600	22	No pH change
Polyvinyl alcohol (Baked at 145°C.)	780	26	No pH change
50% Polyvinyl alcohol, 50% phenol-formaldehyde	100	None	Effluent pH - 12
75% Polyvinyl alcohol, 25% polytetraallylammonium bromide	100	19	Effluent pH - 12
Polytetraallyl-ammonium bromide	70	20-35	
Amberplex A-1 anion membrane (Rohm and Haas)	700	None	
Amberplex C-1 cation membrane (Rohm and Haas)	700	None	
Ethyl cellulose	800	None	
Nylon (Plastex Process Co.)	800	None	

TABLE 1 (Continued)

Membrane Tested	Pressure on Membrane p.s.i.	Semipermeability, % Rejection[a] of Dissolved NaCl by Membrane	Remarks
Cellophane (du Pont PT 300)	700	6	No pH change
Rubber hydrochloride	700	--	No flow through membrane[b]
Polystyrene (Dow Chemical Co.)	800	None	
Saran (Dow Chemical Co.)	800	None	Very slow flow rate
Polyethylene	800	None	
Cellulose acetate butyrate	800	None	
Cellulose acetate (Celanese S-604)	800	--	No flow
Cellulose acetate (du Pont 88 CA-43)	850	96	
Cellulose acetate (du Pont 88 CA-43)	400	97.4	

[a] Percent rejection was based upon the change in chloride concentration from influent to effluent.

[b] If after 48 to 72 hours, no water was collected, an entry of no flow was made.

TABLE 2

SEMIPERMEABILITY OF CELLULOSE ACETATE TO AQUEOUS SOLUTIONS OF VARIOUS ELECTROLYTES

Membrane[a]	Pressure on Membrane p.s.i.	Electrolyte	Concentration[b]	Semipermeability, % Rejection of Dissolved Electrolyte by Membrane
Cellulose acetate	850	NaCl	0.11 M	96
Cellulose acetate	715	$MgCl_2$	0.031 M	99
Cellulose acetate	800	$CaCl_2$	0.0054 M	98
Cellulose acetate	500	Na_2SO_4	0.018 M	97
Cellulose acetate	850	NaBr	0.0012 M	93
Cellulose acetate	840	NaF	0.0012 M	86
Cellulose acetate	800	H_3BO_3	0.0011 M	46
Cellulose acetate	800	NH_3	0.04 M	30
Same film as used for NH_3 experiment	830	NaCl	0.17 M	90
Cellulose acetate	800	Ocean Water	4%	96

[a] Du Pont CA-48 cellulose acetate membrane 0.88 mils thick was used for this series of tests.

[b] Analytical procedures are given in the Appendix.

Before an improved membrane can be developed on a systematic basis, some knowledge of the mechanisms involved in the transfer of water and ions across this membrane is needed.

CHAPTER II

THEORY FOR THE SEMIPERMEABILITY OF CELLULOSE ACETATE

Review of Existing Theories

Of the many theories proposed for the semipermeability of membranes, none adequately explains the semipermeability of cellulose acetate. Several of the more significant theories will be reviewed.

Sieve mechanism.--One of the earliest that was proposed was the sieve mechanism (1). According to this concept, a semipermeable membrane possesses pores intermediate in size between the solvent and solute molecules. Thus the solute molecules would be blocked and the smaller solvent molecules would be allowed to pass. However, several semipermeable membranes have been found in which the pore size is larger than the solute molecules. Our results indicate that the sieve mechanism could not account for the high semipermeability of cellulose acetate. Referring to Table 1, nylon and saran which had much lower flow rates than cellulose acetate (and presumably smaller pores) exhibited no semipermeability under the conditions of the experiment. Furthermore, the difference in size between

polymerized water molecules and sodium or chloride ions is not sufficient to permit the sieve mechanism to apply.

Distillation mechanism.--Another theory is based upon the perfect semipermeability of the surface of a solution (1). If solute molecules (such as NaCl) are not volatile, then only the volatile solvent molecules can penetrate the surface barrier. H. L. Callendar (1) considered that solvent molecules distilled across a semipermeable membrane. Of necessity the walls of the capillaries through which the solvent distills would have to be non-wettable to the solvent or the solution. This requirement renders the theory inapplicable to cellulose acetate, because water has a high affinity for the free hydroxyl groups in the film (17).

Ion exchange mechanism.--In recent years a considerable amount of research has been devoted to ion exchange membranes. These membranes are permselective. That is, they have a very low resistance to the passage of either cations or anions but not both. This selectivity is due to the high concentration of positive or negative charges that are incorporated into the film (18, 19, 20). Consequently, these membranes would be semipermeable if they effectively blocked the passage of either the cation or the anion of the solute and permitted solvent molecules to pass.

It is unlikely that the high degree of salt rejection that cellulose acetate exhibits could be due to an ion exchange mechanism. Cellulose acetate with approximately 40 per cent acetyl content has a low concentration of hydroxyl groups. Thus, according to the theory of Teorell and Meyer-Sievers (19), it would behave only slightly as an ion exchange membrane.

On the basis of the ion exchange theory, the semipermeability of several ion exchange membranes was determined. None of them (i.e. tetraallylammonium bromide, Amberplex A-1 and C-1 in Table 1) exhibited a high degree of semipermeability. McKelvey, in an unpublished report to the National Colloid Symposium in 1956, indicated similar results.

However, a series of experiments was conducted to determine whether or not cellulose acetate actually does behave as a permselective membrane. The results of these experiments, which are reported in Chapter IV, indicate that it does not.

Adsorption mechanism.--A theory of semipermeability based upon the relative adsorption of solvent and solute molecules by the membrane has been proposed (1). Semipermeability results when the solvent molecules are adsorbed positively and the solute molecules negatively adsorbed. This type of semipermeability is most pronounced

when the pore size is small and surface flow predominates (21).

Solubility mechanism.--Closely related to the adsorption theory is the solubility theory. This was first proposed by M. L'Hermite in 1855 (1) and has today gained wide acceptance (17). The theory proposes that semipermeability is an outgrowth of the solubility of the solvent and the insolubility of the solute in the membrane. Since the solvent is soluble in the membrane, it can pass but the solute cannot.

In their most general sense, the solubility and adsorption theories would certainly cover the observed behavior of cellulose acetate. However, this question is then raised: Why is the solubility or adsorption of water in cellulose acetate so much greater than that of strong electrolytes? If it could be attributed merely to the presence of hydrophilic groups, then cellophane and polyvinyl alcohol, which have a very high concentration of hydroxyl groups, should have a greater degree of salt rejection than cellulose acetate does. But as indicated in Table 1, they do not. Therefore, a clearer understanding of the mechanisms involved in the transfer of water and ions across cellulose acetate is needed.

Proposed Mechanism

To formulate a theory which would explain the semi-permeability of cellulose acetate, it was necessary to find out what unique combination of properties of cellulose acetate caused this phenomenon. Fortunately a great amount of work has been done on cellulose chemistry. This work is well summarized in Volume V of High Polymers (17), and pertinent parts of it will be briefly described here before the proposed mechanism is presented.

Cellulose type membranes are made up of a network of long polymers averaging 15,000 Å in length and 5 to 20 Å in width. These polymers have for the most part a random orientation in the membrane. As an analogy, Sollner (18) uses a pile of straw to describe their packing. When polymer chains run parallel to each other in an orderly manner, crystalline regions are set up. In these regions the polymers are held together by hydrogen bonds and van der Waal forces and assume definite spacings. On the other hand, when the chains lie in a disorderly manner, the spaces between polymers are much greater. These are called amorphous regions. The formation of these crystalline regions is a dynamic process. Mark, in High Polymers (17), says that the individual chains are subject to Brownian motion. During a given period within a given

volume, segments of polymer chains will become parallel to each other and assume a high degree of order. Later these crystalline regions will disappear as a result of Brownian motion. Thus the system as a whole has an average degree of order intermediate between complete crystallinity and complete amorphousness.

Compression of a membrane results in a complicated rearrangement of the polymer network. During compression the system goes through many transition states because of the irregular shape of the polymers and the variety of forces that come into play between individual polymer chains. The consolidation of the three-dimensional lattice thus becomes a complicated multi-step process of settling down to an arrangement of highest compactness and stability.

This concept of the internal structure of membranes applies to all types of cellulose films. Baker (22) has shown, however, that cellulose acetate is unique in that it possesses a very high degree of crystallinity. That is, the internal forces are numerous enough and strong enough to restrict Brownian motion and hold a large percentage of the polymer chains in highly ordered regions. Of necessity the spacings in the amorphous regions are much smaller than they would be if there were little or no crystallinity. When water molecules are introduced

into this structure, they are concentrated in the amorphous regions (17).

It is now postulated that these water molecules, through hydrogen bonding, cross-link the polymer chains and fill the voids in the amorphous regions with bound water. The extent of cross-linking depends upon the size of the voids. When they are large, as in the case of cellophane, the structure is weakly cross-linked. When they are small, as in the case of cellulose acetate, the cross-linking is extensive.

Furthermore, when there is a low degree of cross-linking, the voids are only partially filled with bound water leaving holes through which ions can pass. When the network is highly cross-linked there is little or no free space. All of the water is hydrogen bound to the polymer network either directly or through other water molecules. Brownian motion of the cellulose chains would thereby be restricted.

In a structure such as this, it is proposed that two different mechanisms of diffusion occur. Ions and molecules that cannot enter into hydrogen bonding are transported across the membrane by hole-type diffusion. That is, their diffusion depends upon the concentration of holes in the membrane. Cross-linking cellulose polymers with water reduces the probability of hole formation,

thereby reducing diffusion of this type.

Those ions and molecules that can combine with the membrane through hydrogen bonding and can fit into the bound water structure are presumed to be transported across the membrane by alignment-type diffusion. Their diffusion depends upon the establishment of hydrogen bonds with the membrane. After these molecules combine with one side of the membrane, they migrate across by transferring from one hydrogen bonding site to another and are finally discharged from the other side.

Based upon these concepts (i.e. bound water, hole- and alignment-types of diffusion), it can now be deduced that the semipermeability of cellulose acetate is due to this situation: that within the membrane strong electrolytes diffuse very slowly compared to the rate of diffusion of water. In cellulose acetate the high degree of crystallinity reduces Brownian motion and pore size sufficiently to permit bound water to fill the voids which greatly reduces the probability of hole formation. Hence the rate of diffusion of sodium chloride is very low. If the membrane were compressed, more cross-linking would occur, the bound water would become more stabilized, and the rate of diffusion would become even less.

On the other hand, the diffusion rate of water through cellulose acetate is relatively high since it is

transported by a different mechanism. Compression of the membrane would not be expected to reduce appreciably alignment-type diffusion of water. Therefore, compression of the structure should increase the semipermeability of the membrane.

The hydrogen bonding mechanism does not exclude the sieve mechanism. The size of the holes that are continually appearing and disappearing plays a secondary role. The rates of diffusion of solutes that cannot enter into hydrogen bonding depend upon pore size. However, in the case of those ions and molecules that can enter into hydrogen bonding, the permeability depends upon their ability to fit into the ice-like structure of the membrane.

Literature Support for Theory

Cellulose acetate provides excellent conditions for hydrogen bonding because there are large numbers of oxygen atoms in each polymer. That water is bound to cellulose acetate polymers is amply supported in the literature. Gruner (23), Petitpas (24), and others (17) have discussed chemical type bonding between water and cellulose polymers. It has been reported by Davidson (25) that the density of the sorbed water along the boundaries of crystalline regions is 5 to 7 per cent higher than water at atmospheric pressure. This corresponds to a pressure of 2000 kg./cm.^{2}

If water were passing through cellulose acetate by combining with the bound water within the membrane, its reduction in entropy should be comparable to the conversion of liquid water to ice. Stamm and Loughborough (26) report that the first water sorbed by cellulose acetate has a $T\Delta S$ value equivalent to the heat of fusion of water indicating that the water does have orientation (and hence bonding) comparable to that of ice. Neale (27) has also reported that the bonding between cellulose and water is comparable to that of ice.

The work of Baumgarth (9) on ultrasonics suggests that strong electrolytes migrate in cellophane by hole-type diffusion. He observed that the rate of diffusion of NaCl in cellophane was increased two-fold by the action of ultrasonics. The ultrasonic acoustical radiation increased the vibration of the cellulose polymers and this might be expected to increase the concentration of holes in the polymer. Consequently, hole-type diffusion would be increased.

Henser (29) makes the point that the hydroscopicity of cellulose derivatives depends upon the geometrical arrangement of the cellulose molecules. This indicates that any molecules that penetrated cellulose acetate membrane by hydrogen bonding would have to be sterically compatible with the water-cellulose acetate structure.

CHAPTER III

EXPERIMENTAL SUPPORT OF THEORY BASED UPON SEMIPERMEABILITY DETERMINATIONS

Although there is abundant evidence to substantiate indirectly the theory presented in the previous section, little experimental work has yet been reported to support it directly. Consequently, a series of experiments was designed to test this concept. These experiments fall into two broad categories. The first group was based upon the determination of the semipermeability of cellulose acetate under various conditions. They are reported in this chapter. The second group of experiments was based upon the measurement of the electrical properties of cellulose acetate under various conditions. These experiments are reported in the following chapter.

The hydrogen bonding concept is compatible with the results contained in Table 2. To facilitate an explanation, the semipermeability will be expressed as:

$$\text{Semipermeability} \sim \frac{\text{Rate of diffusion for solvent molecules}}{\text{Rate of diffusion for solute molecules}} \quad (1)$$

The relationship between the rate of diffusion of salt molecules and the rates of diffusion of the individual

ions is not clear. However, the following general relationship would be expected. An increase in the diffusion rate of either one or both ions of a salt would result in an increase in the diffusion rate of the salt.

In the foregoing expression, perfect semipermeability corresponds to infinity, whereas, when semipermeability is expressed in terms of per cent salt rejection, perfect semipermeability corresponds to 100 per cent salt rejection.

Inasmuch as neither the cations nor the anions of NaCl and NaBr can enter into hydrogen bonding, these salts should be effectively rejected, and they are. The very high rejection of $MgCl_2$ and $CaCl_2$ may be attributed to the large size of the hydrated magnesium and calcium ions which would reduce their rate of diffusion.

Since the fluoride ion can enter into hydrogen bonding, this ion should have a greater rate of diffusion than the chloride ion. Sodium fluoride, therefore, should have a lower semipermeability than NaCl, and this was found to be true.

A very low salt rejection would be expected for those solutes that can enter into the water-cellulose acetate structure through hydrogen bonding. Ammonia is an example of this type of solute. As indicated in Table 2, the semipermeability for NH_3 was only 30 per cent--about a third of that for NaCl.

Apparently the H_3BO_3 molecule can enter into the water-cellulose acetate structure with considerable ease, because its salt rejection was 46 per cent.

The mechanism presented in Chapter II is also compatible with the results presented in Table 1. Polyvinyl alcohol and cellulose both have large concentrations of oxygen atoms that permit cross-linking via hydrogen bonding. However, the degree of crystallinity of these two polymers is low; consequently, there is much Brownian movement and the concentration of holes is relatively large. For this reason these membranes have a low degree of semipermeability.

For this same reason, cellulose acetate butyrate and ethyl cellulose exhibit no semipermeability. Spence (30) has shown that because of the plasticizing effect of the butyrate group, cellulose acetate butyrate has a much lower degree of crystallinity than cellulose acetate.

Effect of Pressure on Semipermeability

When the semipermeability of cellulose acetate (expressed as per cent salt rejection) was determined at various pressures, the relationship depicted in Figure 2 was obtained. An explanation for this phenomenon has already been suggested. As pressure is applied, the Brownian movement is restricted and the "pile of straw" is compressed.

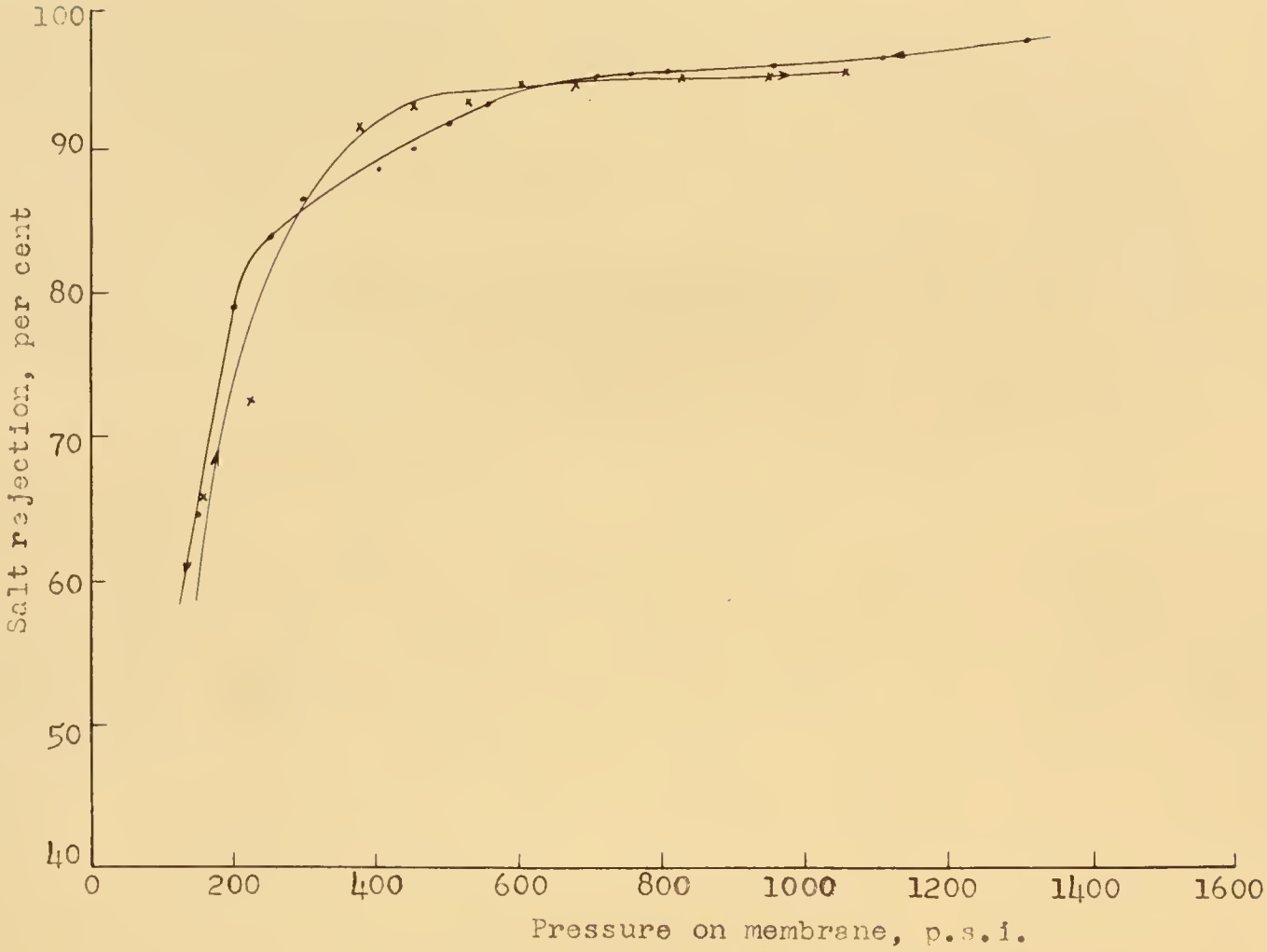

Fig. 2.--Effect of pressure on the semipermeability of 40 per cent cellulose acetate membranes.

Much more cross-linking by water then becomes possible and the membrane becomes a more impenetrable barrier to sodium chloride.

Effect of Crystallinity on Semipermeability

Spence (30) has also shown that as the acetyl content of cellulose acetate is increased, the degree of crystallinity likewise increases. Varying the acetyl content then becomes a means of varying the crystallinity.

Increasing the degree of crystallinity would have a two-fold effect according to the hydrogen-bonding mechanism. First, as explained in Chapter II, the semipermeability should increase. Second, the flow rate of water through the membrane should decrease since the percentage of amorphous regions (through which the water passes) is decreased.

Variations of salt rejection and flow rate with acetyl content have been determined. They are presented in Figures 3 and 4 respectively. The procedure used in preparing the membranes is given in the Appendix.

The role of crystallinity as depicted above is borne out by the data. Up to an acetyl content of 40 per cent there was a continual increase in the semipermeability and a decrease in the penetration of water.

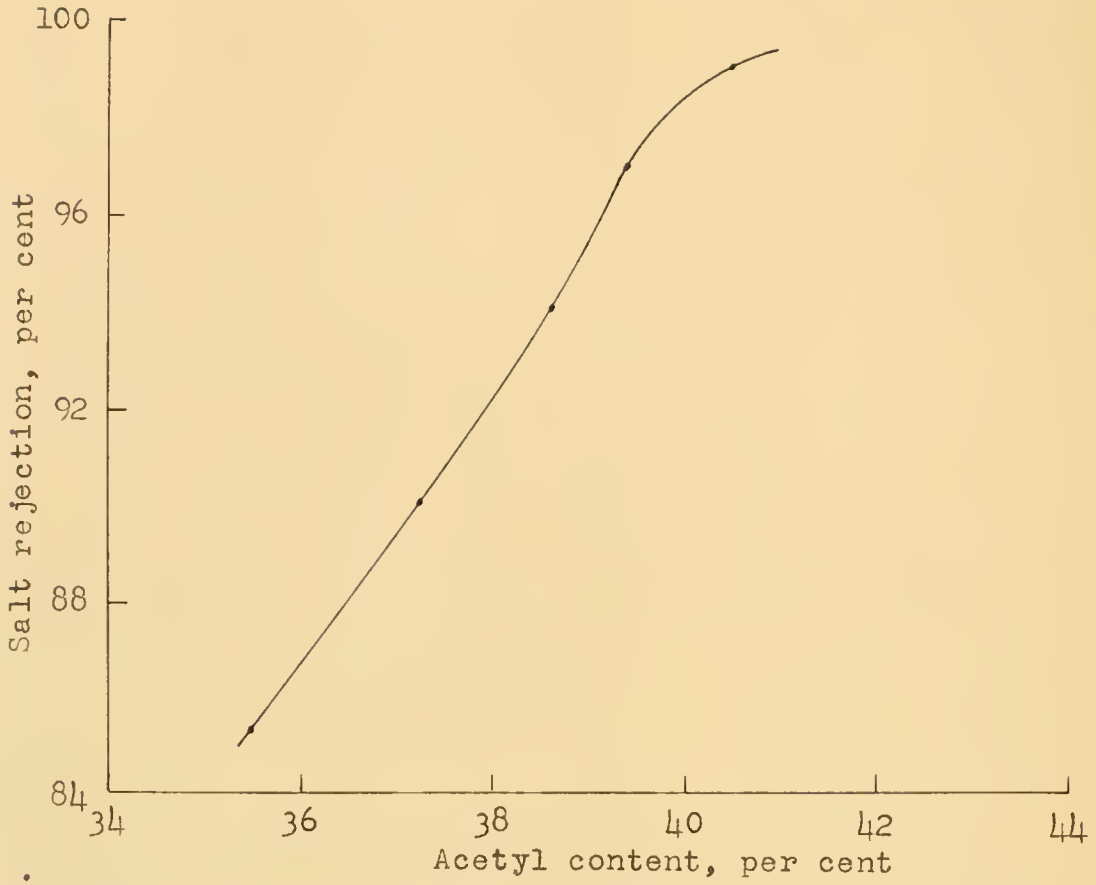

Fig. 3.--Effect of Acetyl Content on Salt Rejection

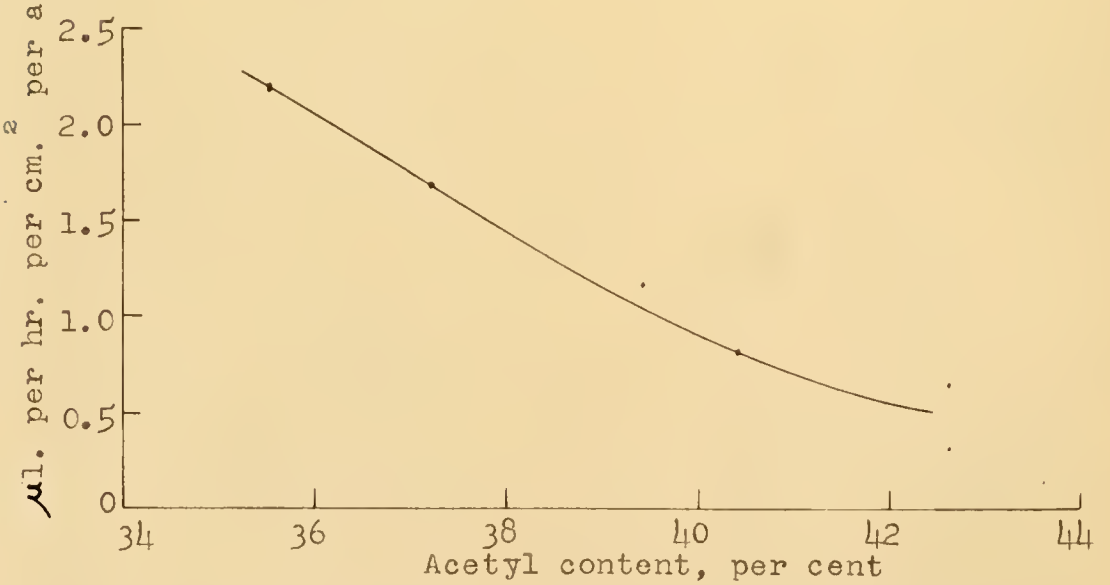

Fig. 4.--Effect of Acetyl Content on Flow Rate

CHAPTER IV

ELECTRICAL MEASUREMENTS TO SUPPORT THEORY

In the previous chapter semipermeability-type experiments were described which support the hydrogen bonding concept of semipermeability. However, these experiments support only indirectly the crux of the theory--namely that hydrogen bonding sets up an ice-like structure impenetrable to strong electrolytes. More direct evidence was needed--first, to establish the existence of the bound water regions and second, to show that two different types of diffusion are involved in the transfer of water and sodium chloride ions across cellulose acetate.

Dielectric Measurements of Cellulose Acetate

Evidence for the existence of the water-cellulose acetate structure could be obtained by showing that compression of the membrane which sets up the structure and increases the amount of bound water is accompanied by an increase in hydrogen bonding. In order to detect an increase of hydrogen bonding, some observable property which depended upon hydrogen bonds was needed. The dielectric

constant meets this requirement. It has been established that hydrogen bonding markedly increases the dielectric constant of some liquids. Pauling (31) has explained this effect on the basis that hydrogen bonding increases the dipole moment which in turn increases the dielectric constant.

Latimer (32) on the other hand explains this effect on the basis of atomic polarization. He presents arguments to show that the polarization of hydrogen atoms involved in hydrogen bonding causes a large contribution to the dielectric constant. Furthermore, using Raman spectra, he shows that the largest contribution to the dielectric constant is made when the axis of the hydrogen bond is parallel to the field intensity.

If Latimer's concept is correct, the dielectric constant of hydrated cellulose acetate should increase with pressure since the amount of bound water is also increasing. If no additional hydrogen bonding were occurring when cellulose acetate is compressed, the dielectric constant of hydrated cellulose acetate should remain constant.

The relationship between the increase in dielectric constant and pressure for cellulose acetate is given in Figure 5. Experimental details are included in the Appendix. As shown, there was a decided increase in dielectric constant with pressure. This large increase in dielectric

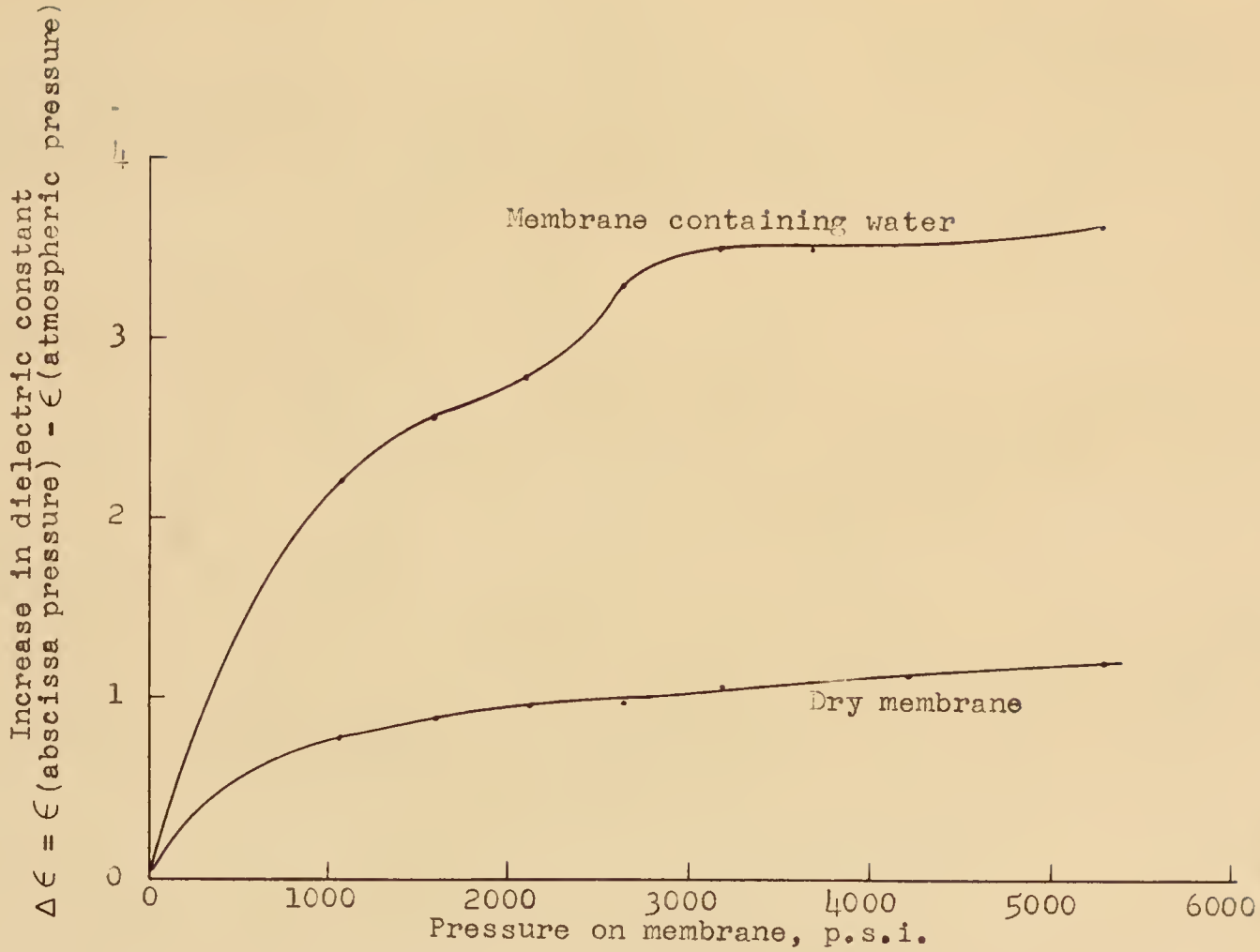

Fig. 5.--Effect of pressure on the dielectric constant of cellulose acetate (du Pont CA-43).

constant is due not only to the formation of hydrogen bonds, but also to the large probability that they are formed in a direction parallel to the electric field intensity.

It is felt that these results furnish direct evidence of the existence of bound water regions in cellulose acetate.

Electrical Resistance Across Cellulose Membrane

Hole-type and alignment-type diffusion in cellulose acetate.--Electrical resistance measurements were used to demonstrate that two different types of diffusion are occurring in cellulose acetate. In electrolytic conduction the current is carried by anions and cations in solution. Both electrical resistance and rate of diffusion depend upon the mechanical resistance that these ions encounter during migration. Therefore the electrical resistance across a membrane can serve as a quantitative index of their diffusion rates. Diffusion rate and electrical resistance, of course, vary inversely with each other. In subsequent sections the term membrane resistance refers to the electrical resistance across the membrane.

The membrane resistance of a specific ion can be determined by placing an appropriate ion exchange membrane on each side of the semipermeable membrane. The procedure is given in the Appendix. The membrane resistance of water

molecules was approximated by determining the resistance of hydronium ions (H_3O^+).

The electrical resistances for Na^+, Cl^-, NaCl, and H_3O^+ across cellulose acetate as a function of pressure is plotted in Figure 6. At atmospheric pressure the resistances of Na^+, Cl^-, and NaCl are much higher than the resistance of H_3O^+. Further, as the membrane is compressed, the resistance of H_3O^+ remains relatively constant whereas the resistances of Na^+, Cl^-, and NaCl rapidly increase.

Considered in terms of diffusion, this indicates that at atmospheric pressure the diffusion rates of Na^+ and Cl^- which cannot enter into hydrogen bonding were very low and became even lower when the membrane was compressed. In contrast, the diffusion rate of H_3O^+ which can enter into hydrogen bonding was relatively high at atmospheric pressure and was only slightly reduced when the membrane was compressed.

It is considered that these results furnish strong direct evidence to show that those ions and molecules that cannot combine with cellulose acetate diffuse by a different mechanism than those ions and molecules that can combine with the membrane through hydrogen bonding.

Relationship between membrane resistance and semipermeability.--In Chapter III a qualitative expression was given relating to semipermeability, the diffusion rate

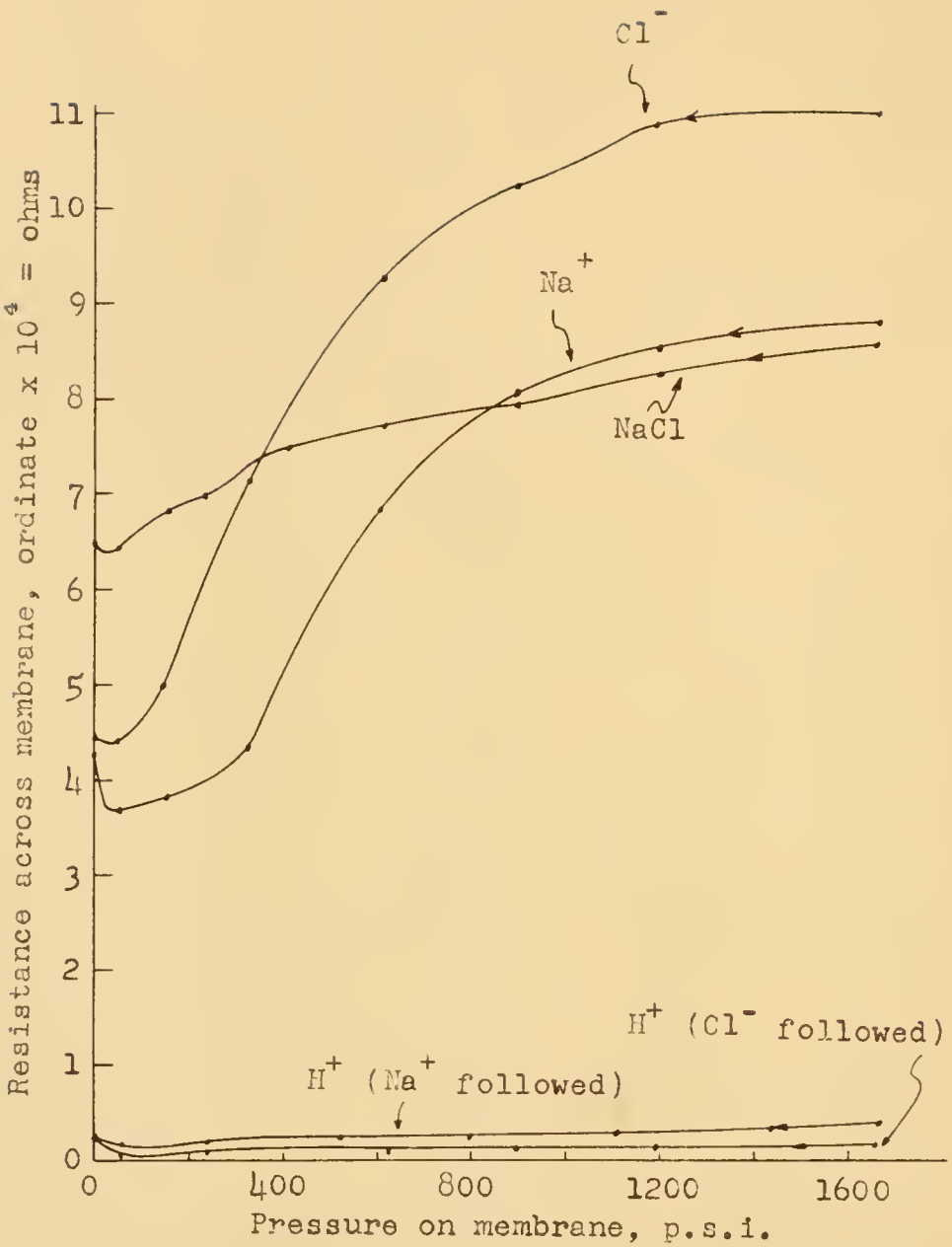

Fig. 6 .--Resistance versus pressure across 40% cellulose acetate membrane.

of solvent molecules, and the diffusion rate of solute molecules. Bearing in mind the inverse relationship between diffusion rate and membrane resistance, this expression may be written as:

$$\text{Semipermeability} \sim \frac{\text{Membrane resistance for solute molecules}}{\text{Membrane resistance for solvent molecules}} \quad (2)$$

That semipermeability does vary with the resistance of the solute is borne out by a comparison of Figures 2 and 6. The rate of increase of semipermeability with pressure given in Figure 2 corresponds to the rate of increase in resistance of the solute given in Figure 6. It can also be deduced from Figure 6 that in the case of an ionized solute, the semipermeability depends largely upon the ion with the higher membrane resistance. Note that the increase in semipermeability with pressure corresponds more closely to the increase in Cl^- resistance with pressure than with that of either Na^+ or NaCl.

To provide further evidence that semipermeability is related to membrane resistance, the resistances of membranes with high and low semipermeabilities were determined. It can be seen from Figure 7, in which these runs are compared, that the membrane with a high semipermeability also had high electrical resistance, and the membrane with a low semipermeability had a low resistance that did not increase with pressure.

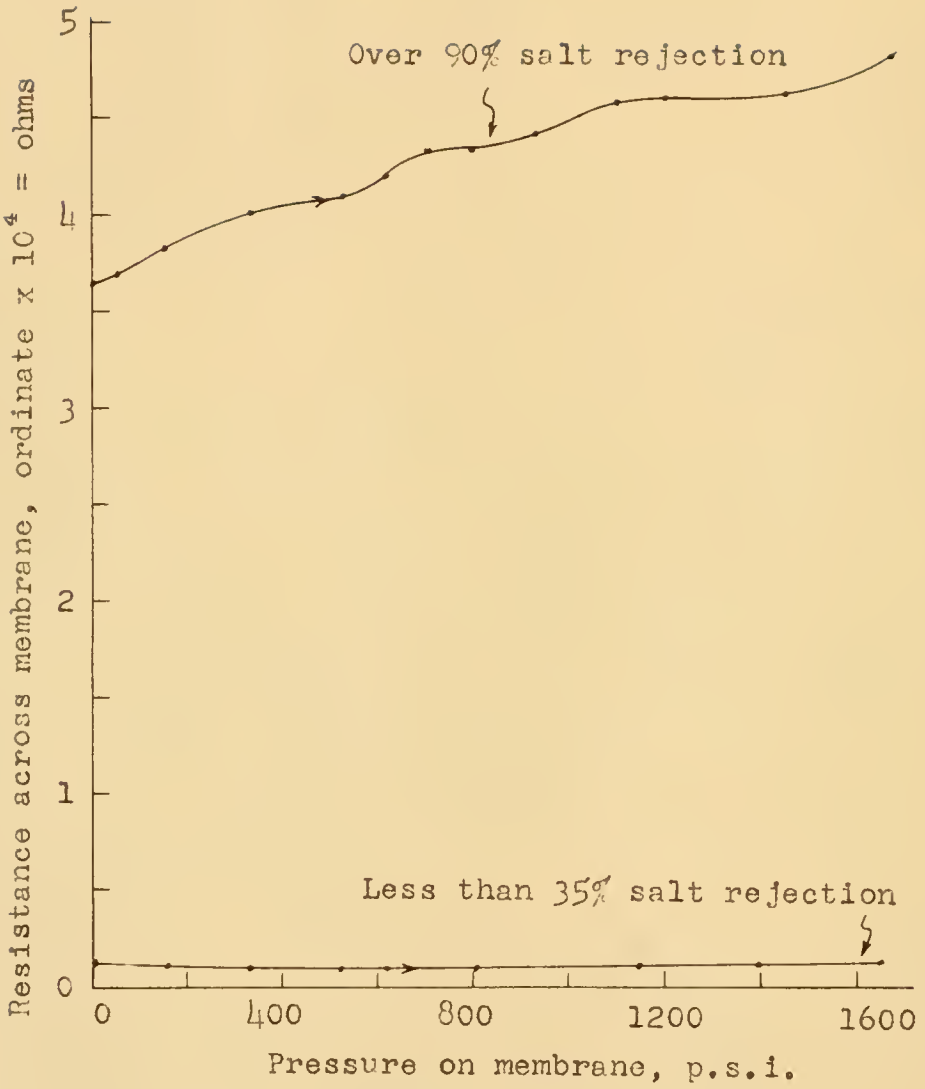

Fig. 7.--Resistance versus pressure for sodium chloride across cellulose acetate membranes (du Pont CA-43) of known salt rejections.

Effect of bound water on hole-type diffusion.--In a previous section dielectric constants were used to show that compression of cellulose acetate sets up regions of bound water. In the two preceding sections membrane resistances were used to show that compression of cellulose acetate causes the rate of hole-type diffusion to decrease. A comparison of dielectric constants and membrane resistances as a function of pressure illustrates that the formation of bound water regions restricts hole-type diffusion. Such a comparison is made in Figure 8. The lower curve in Figure 8 represents the increase in hydrogen bonding with pressure. The close resemblance of this lower curve to the resistance curve of Cl^- indicates very strongly that the hydrogen-bound water-cellulose acetate structure is responsible for the high membrane resistance or low diffusion rate of strong electrolytes.

The shift of the resistance versus pressure curve to the left was probably the result of a hysteresis effect as the pressure was reduced.

Semipermeability of cellophane.--It was mentioned in Chapter III that the low degree of semipermeability of cellophane is attributable to its low degree of crystallinity. A certain amount of energy is required to overcome the Brownian motion of the cellulose polymers and to compress the system so that a cross-linked water-cellulose

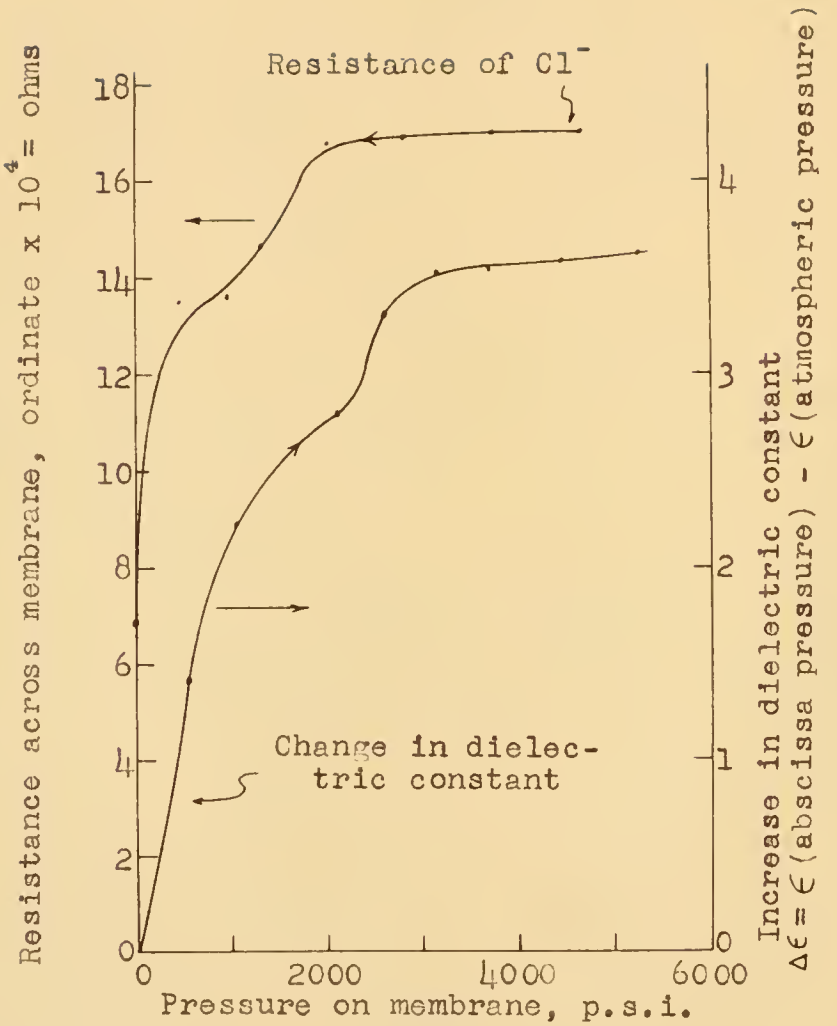

Fig. 8.--Comparison of semipermeability and dielectric constant of cellulose acetate membranes.

structure can be set up. Crystallinity supplies energy required for the formation of the desired structure. Cellulose acetate has a high degree of crystallinity, so only little additional pressure is needed to set up the bound water structure. With cellophane, however, much additional pressure is needed to accomplish the same result.

To learn whether or not the semipermeability of cellophane increases at higher pressures, the membrane resistances of H^+, Na^+, Cl^-, and NaCl were determined up to 5500 p.s.i. These results are presented in Figure 9. The membrane resistance of H_3O^+ remained relatively constant. The resistance of Cl^-, however, increased rapidly. Therefore the semipermeability of cellophane should increase with pressure.

The semipermeability of cellophane was determined up to 1500 p.s.i. The salt rejection of cellophane did increase from about 8 per cent at 600 p.s.i. up to 14 per cent at 1500 p.s.i. (33).

Effect of temperature.--Another type of experiment was conducted to determine if hydrogen bonding was connected with membrane resistance. It is recognized that hydrogen bonds are very sensitive to temperature. At lower temperatures the hydrogen bonding is greatly increased. For example, at 4°C. water is more polymerized than at room temperature.

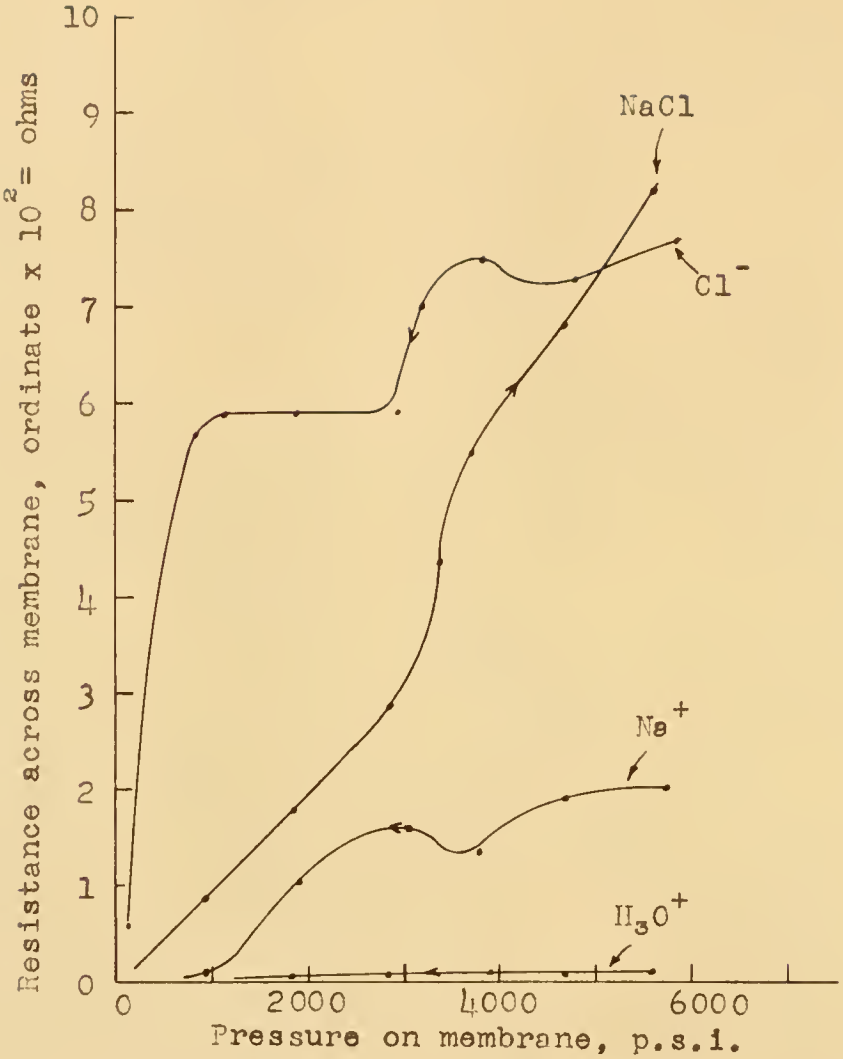

Fig. 9.--Resistance versus pressure for cellophane (du Pont PT-300).

Consequently, increasing the temperature should decrease the semipermeability by breaking up bound water regions and, conversely, decreasing the temperature should increase the semipermeability. The former is illustrated in Figure 10. The temperature was elevated by increasing the passage of current through the membrane. By introducing four times as much heat into the membrane, the change in electrical resistance between 0 and 600 p.s.i. was decreased from 3600 ohms to 350 ohms.

To show the effect of decreasing the temperature, resistance versus pressure determinations for cellophane are given in Figure 11. The temperature was lowered by packing the entire resistance cell in ice. Lowering the temperature had two effects. The overall resistance was increased and the rate of change of resistance with pressure was also increased. This effect of temperature on membrane resistance shows in another way that hydrogen bonding sets up regions that restrict the diffusion of strong electrolytes.

Effect of ions in the water-cellulose acetate structure.--In the course of determining membrane resistances, an unexpected phenomenon was observed. This is illustrated in Figure 12. A cellulose acetate membrane was soaked in water, placed in the resistance cell, and compressed to 7500 p.s.i. After compression, the current was turned on and resistance measurements were made periodically as the pressure was

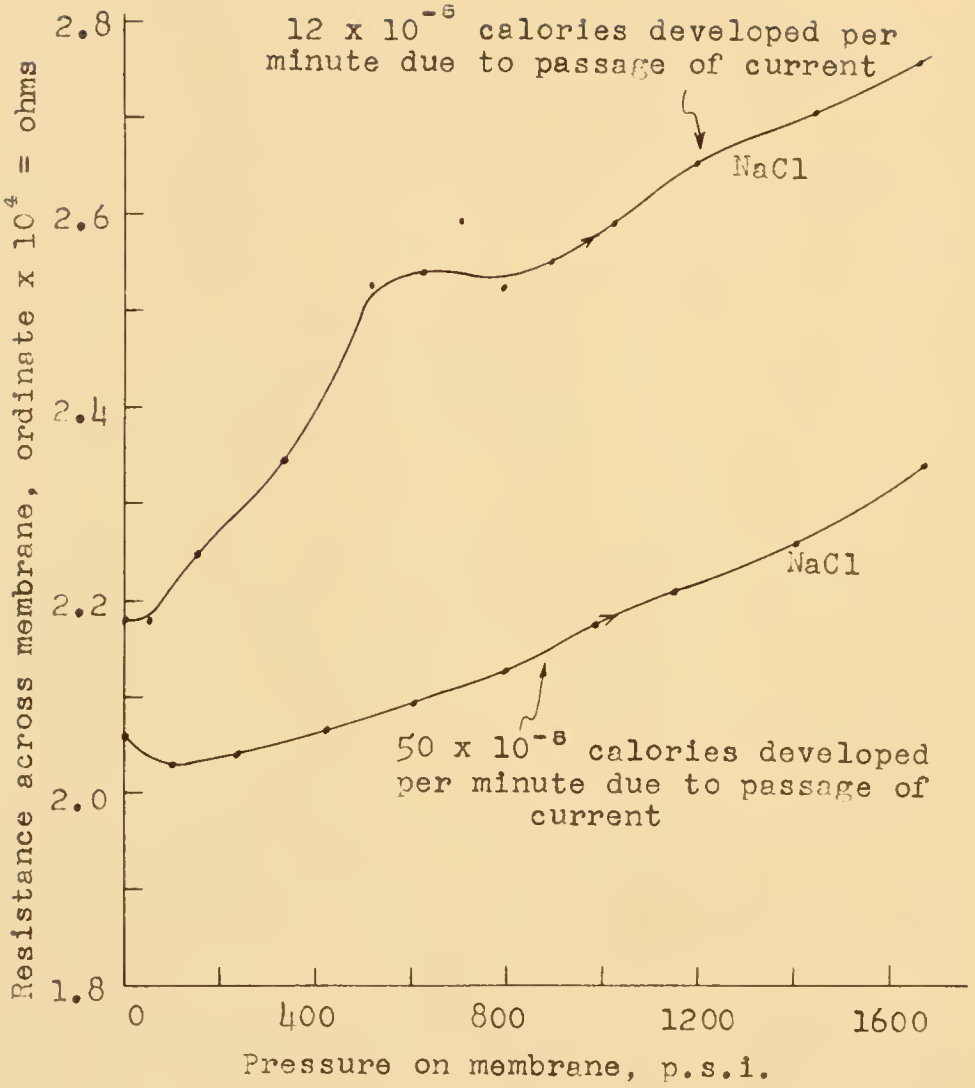

Fig. 10.--Resistance versus pressure for cellulose acetate membrane (du Pont 88 CA-43) with a known salt rejection of over 90%.

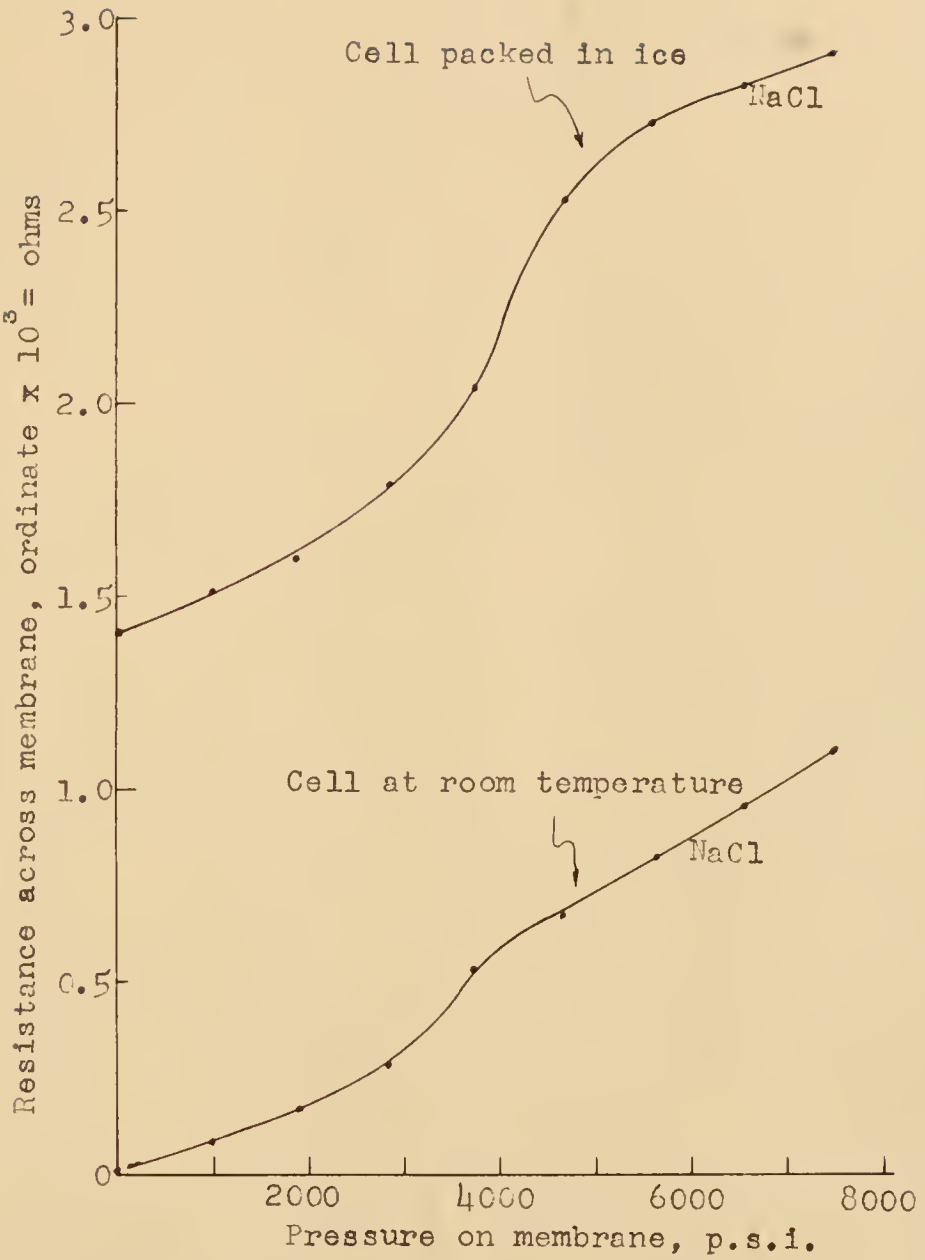

Fig. 11.--Effect of temperature on membrane resistance of cellophane (du Pont PT-300).

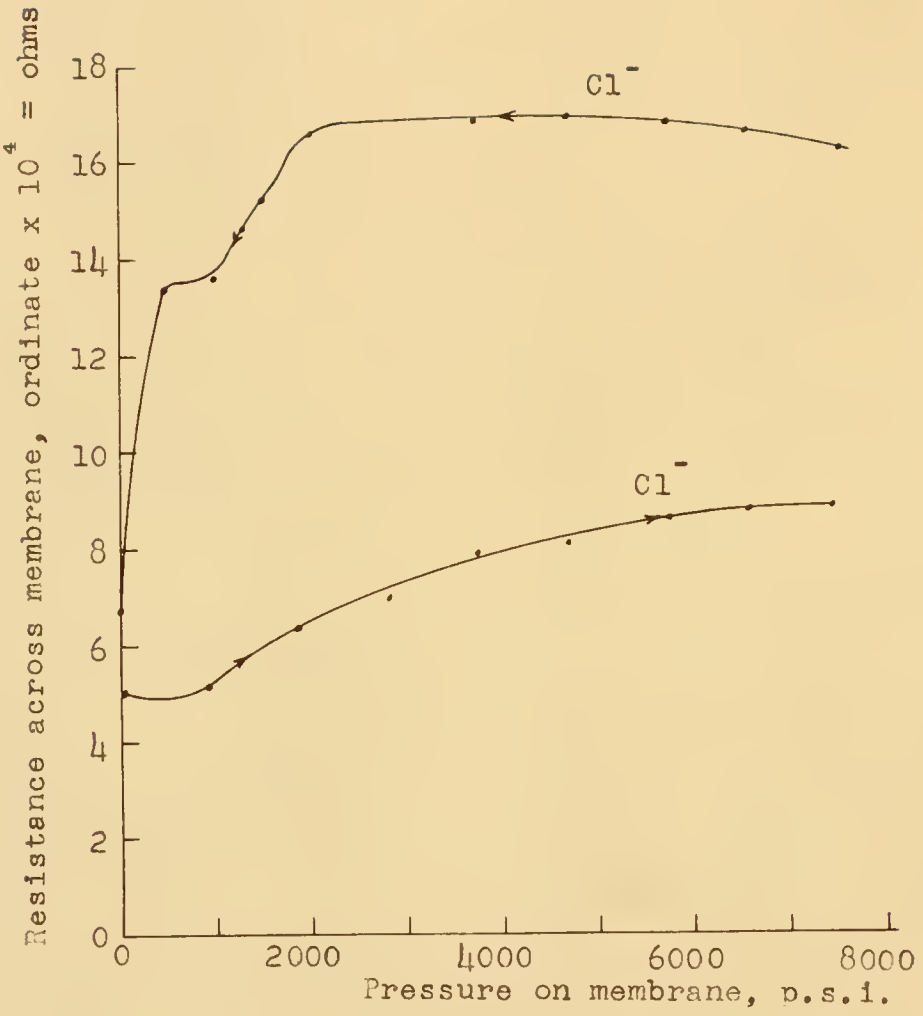

Fig. 12.--Resistance versus pressure for 40% cellulose acetate film. No previous cycles.

lowered to 0 p.s.i. The upper curve was obtained. But when the resistance measurements were made as the pressure was increased, the lower curve was obtained.

It is felt that this effect may be caused by sodium ions lodged in the membrane. To allow chloride ions to be electrically forced through the membrane, electrical neutrality within the membrane must be maintained. This is accomplished by the leakage of sodium ions through the high resistance anion exchange membrane into the cellulose acetate membrane. Once inside the cellulose acetate membrane, the sodium ions are relatively immobile because of the very high cation resistance of the anion exchange membranes. It is considered likely that the presence of these sodium ions disrupts the formation of bound water regions.

Now consider Figure 12 in the light of this explanation. When the membrane was first compressed to 7500 p.s.i. no sodium ions were present so the bound water regions readily formed. The membrane resistance was then able to reach 96,000 ohms. On the other hand, starting resistance measurements at atmospheric pressure introduced large numbers of sodium ions into the structure before the bound water regions were completely developed. These sodium ions then disrupted the continued growth of the bound water regions when the pressure was increased. Consequently at 7500 p.s.i. the membrane resistance had increased to only 37,000 ohms.

It appears that the water-cellulose acetate structure can be broken down at sufficient pressures. Referring again to Figure 12, it can be seen that the membrane resistance begins to decrease at pressures above 4000 p.s.i. In Figure 13 the effect is more pronounced. A du Pont CA-43 cellulose acetate membrane was used. The breaks in the Na^+ and Cl^- curves at 3000 p.s.i. are attributed to the weakening of the water-cellulose acetate structure by sodium and chloride ions. Beyond 3000 p.s.i. the weakened structure begins to fail. On the other hand, the membrane resistance of NaCl, which was determined last, continued to increase up to 5500 p.s.i.

The difference between the resistance curves of NaCl and its ions might be explained in the following way: In the determination of the membrane resistance of NaCl, both ions are free to migrate out of the membrane into the solution. Since both ions are mobile, the formation of the water-cellulose acetate structure would not be inhibited or weakened. In the measurement of the resistances of Cl^- or Na^+, either Na^+ or Cl^- is immobilized within the membrane. These immobile ions may then weaken the water-cellulose acetate structure.

It should be mentioned that the shapes of the resistance versus pressure curves for du Pont cellulose acetate varied widely from sample to sample. This difference

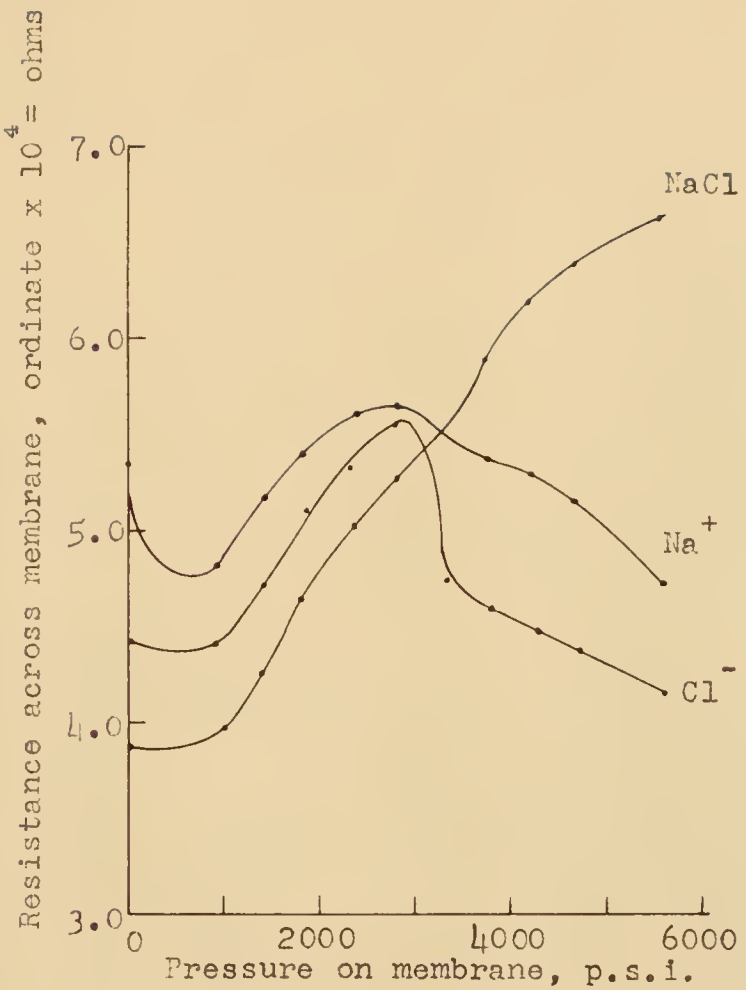

Fig. 13.--Resistance versus pressure across cellulose acetate (du Pont CA-43).

between the resistance curves of NaCl and its ions was in general repeated. The erratic behavior of the commercial films could be caused by the presence of plasticizers. Good reproducibility was obtained with the cellulose acetate membranes prepared in this laboratory--no plasticizers were used.

Effect of pressure on transference numbers.--Originally the intention was to test the proposed mechanism of semipermeability by determining the transference numbers of various ions across cellulose acetate. Transference numbers at elevated pressures were needed. The apparatus that was used for measuring membrane resistances was originally designed for measuring transference numbers. Employing the Hittorf method, the transference numbers for Na^+ and Cl^- across cellulose acetate were determined at pressures up to 4000 p.s.i. No reproducibility or correlation of results could be obtained. The difficulty was traced to the heating effect of the current passing through the membrane. To reduce the current sufficiently to eliminate temperature effects would have made the experiment prohibitively long. It was then decided to employ membrane resistances for testing the theory.

It is still of interest to observe what effect pressure has on the transference numbers of Na^+ and Cl^- in cellophane and cellulose acetate. Basically, transference numbers depend upon the relative electrical

resistances of the ions in the system. For example, in an aqueous sodium chloride solution, the electrical resistance for sodium ions is greater than that of chloride ions. When the solution is conducting electricity, the migration of sodium ions accounts for only 38.5 per cent of the current. The transference number of Na^+ (t_{Na^+}) is then 0.385 and that of Cl^- is 0.615. If the resistance for chloride ions increased, its transference number would decrease.

Thus it seems that the resistance-pressure relationships which have been described previously should serve as a basis for predicting (qualitatively) the variation of transference numbers with pressure.

From these resistance versus pressure measurements it appears that transference numbers within cellophane and cellulose acetate are dependent among other things upon the water-cellulose structure. To illustrate, in Figure 9 at 6000 p.s.i., the resistance of Cl^- is very high compared to Na^+; therefore, the transference number of Cl^- (t_{Cl^-}) across cellophane at this pressure is very much smaller than t_{Na^+}. As the pressure on the membrane is decreased below 1000 p.s.i., the resistance of Cl^- decreases very rapidly which in turn results in a sharp increase in t_{Cl^-}. Neale (34) has found that at atmospheric pressure the transference number of Cl^- across cellophane is of the order of 0.4 in a 0.1 N NaCl solution.

It might be concluded, then, that the formation of the water-cellulose structure causes the transference number of Na^+ to increase. The hydrated Na^+ must be able to fit into the water-cellulose structure with greater ease than Cl^- can.

The transference number of sodium ions across cellulose acetate that had not previously been compressed is less than the transference number of chloride ions. Note from Figure 14 that for this membrane the resistance to Na^+ is greater than that to Cl^-. Yet after measuring the membrane resistance for H_3O^+ up to 1600 p.s.i, the situation is reversed. The transference number of Na^+ is now greater than that of Cl^-. Referring back to Figure 6, the resistance of Na^+ is seen to be appreciably lower than that of Cl^-. The effect of hydrogen ions is to set up the water-cellulose acetate structure. This increase in t_{Na^+} caused by the passage of H_3O^+ through the membrane indicates again that sodium ions can preferentially diffuse through the water-cellulose-type structure.

The significance of this work is two-fold. First, it shows that the semipermeability of cellulose acetate is not caused by an ion exchange mechanism. Had the semipermeability been due to an ion exchange reaction, there would have been a very large difference in resistance between Na^+ and Cl^-. Second, it illustrates the dependence of transference numbers on the internal structure of a membrane.

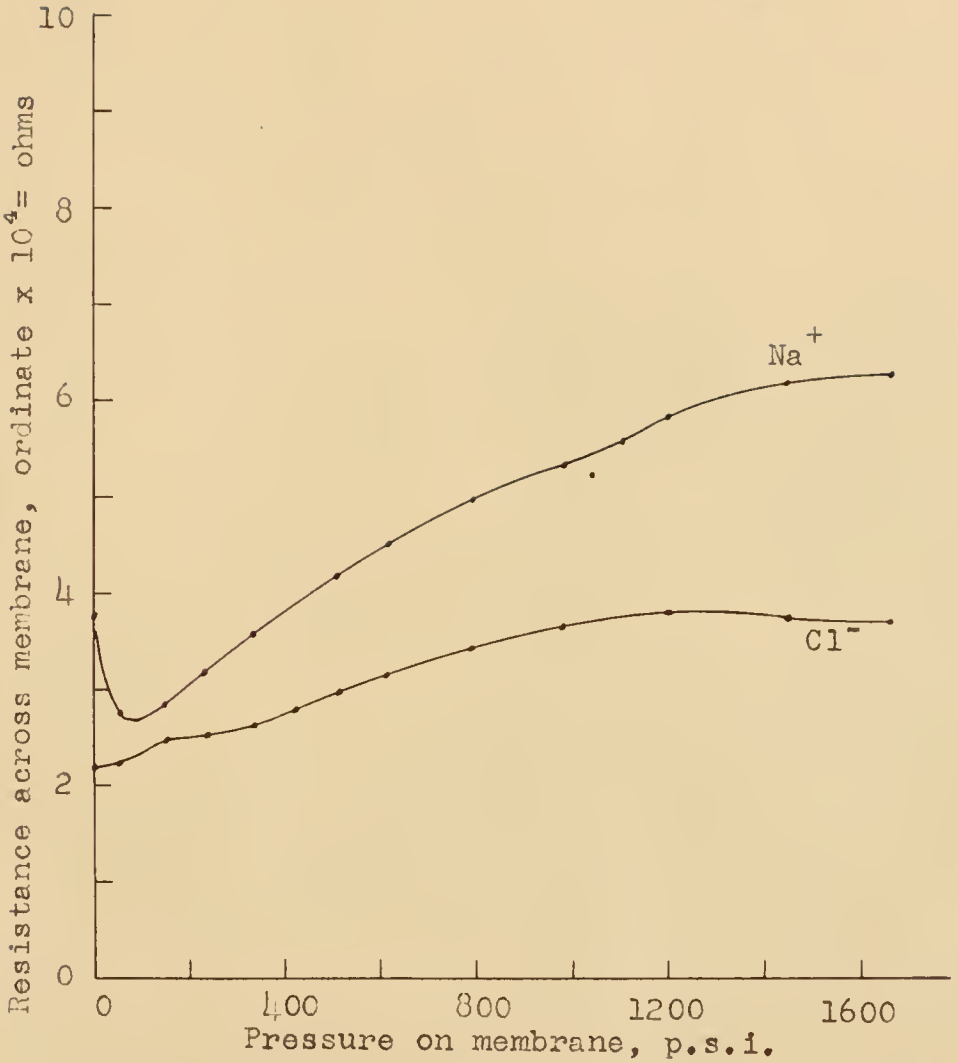

Fig. 14.--Resistance versus pressure across 40% cellulose acetate. Resistances of Na^+ and Cl^- were determined across separate unused membranes.

CHAPTER V

MECHANISM FOR LOSS OF MEMBRANE SEMIPERMEABILITY

In Chapter I mention was made of the fact that cellulose acetate lost its semipermeability after a limited period of time. On the basis of the bound water theory of semipermeability and the results of a series of experiments, a mechanism for membrane failure is proposed.

The experiments that are first described illustrate the nature of the film failure. The next set of experiments shows that chemical reactions between the solute and membrane are involved. And the final group of experiments shows the effects of these chemical reactions on the crystallinity and polymer orientation in the membrane.

Loss of Semipermeability

In order to study the nature of film failure, cellulose acetate films containing 37 per cent combined acetyl content were employed. By using cellulose acetate films with a low acetyl content, the length of the durability tests was reduced. The concentration of all solutes was approximately 0.08 N NaCl. The apparatus and procedure described in Chapter I were used.

Plots of semipermeability versus time and volume of water passing through the membrane are presented in Figures 15 and 16 respectively. In Figure 17 the relationship between time and the rate of diffusion of water through the membrane is given. Two methods of film preparation were employed. Both membranes were cast from the same acetone solution, and the solvent was allowed to evaporate at room temperature. In one case, however, the remaining traces of solvent were removed by forcing water through the film and in the other this was accomplished by heating. These two methods of film preparation are compared in Figures 15, 16, and 17.

Several observations can be made from the data illustrated in these figures. First, the results indicate that not all of the amorphous regions are available for supporting a network of bound water. This is shown in Figure 17. Removal of the solvent by water extraction increased the diffusion rate of water seven-fold over that of the heat-dried film.

This difference in diffusion rates might be explained in the following way: When the solvent is removed by heating, the cellulose acetate polymers lying in non-crystalline regions apparently become bound together by intermolecular forces which prevent them from being used for maintaining oriented water; whereas, when the solvent

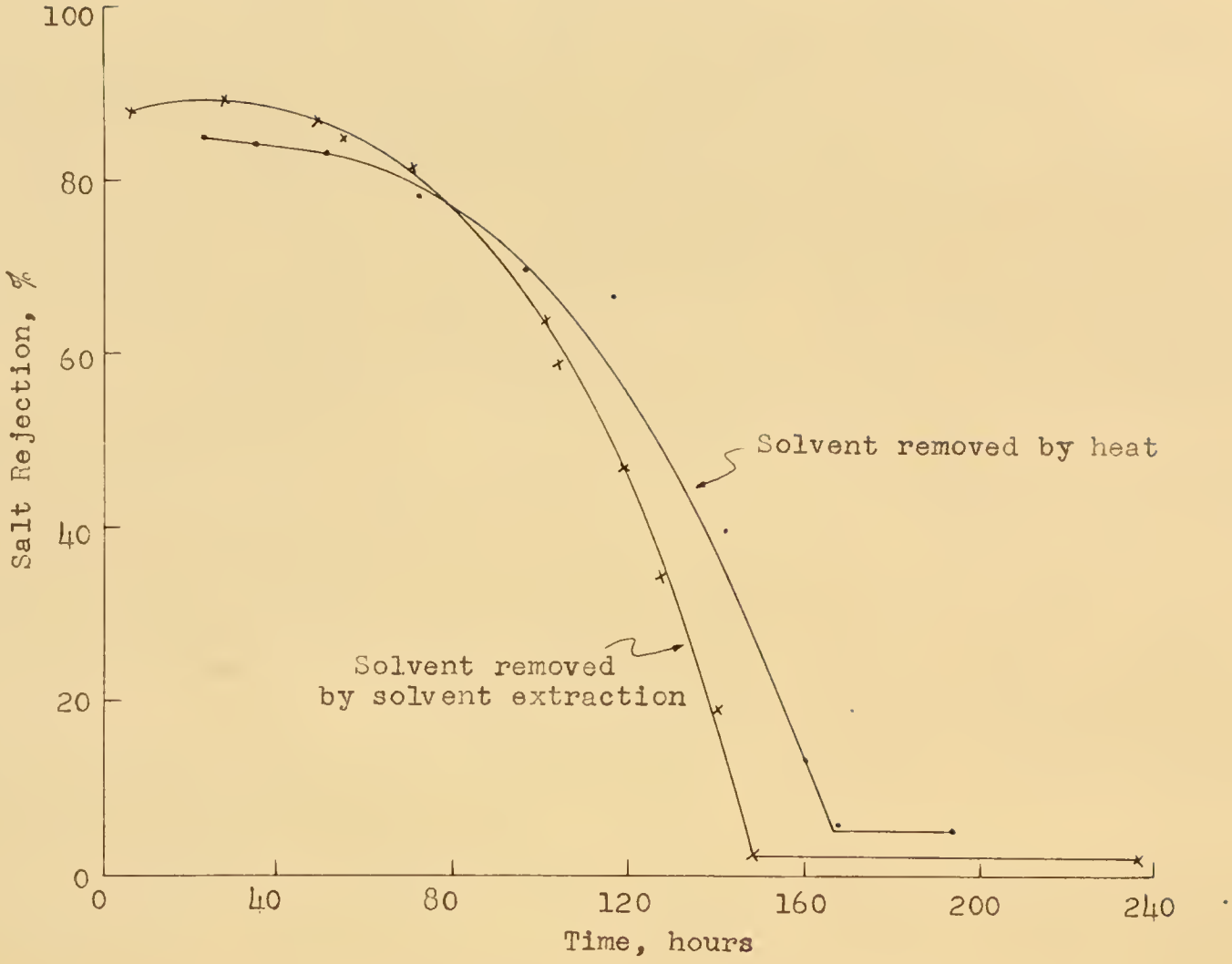

Fig. 15.--Effect of method of removing solvent on the durability of 37.2% cellulose acetate membranes.

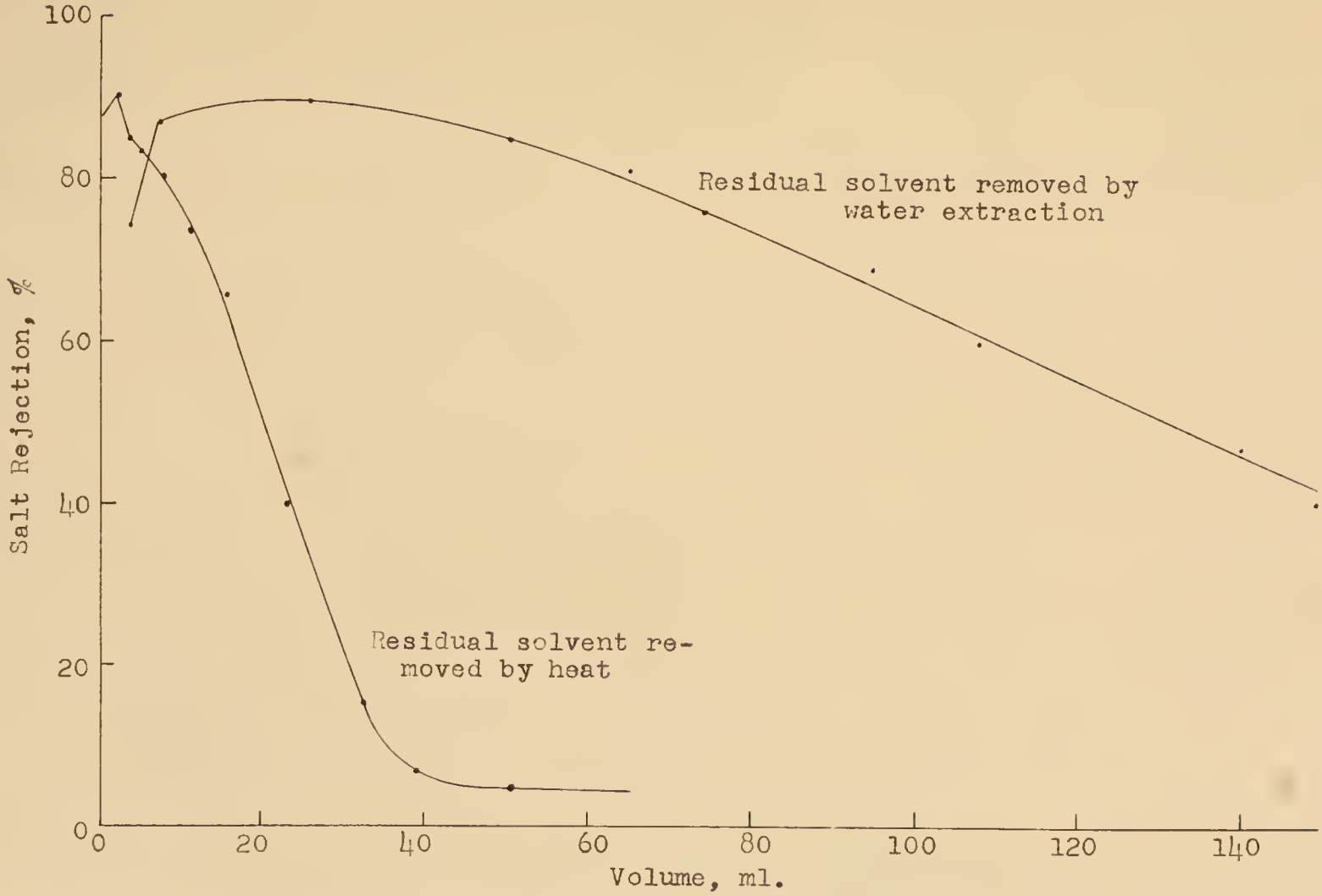

Fig. 16.--Effect of method of removing solvent on the variation of salt rejection with volume. Cellulose acetate containing 37.2% combined acetyl content was used.

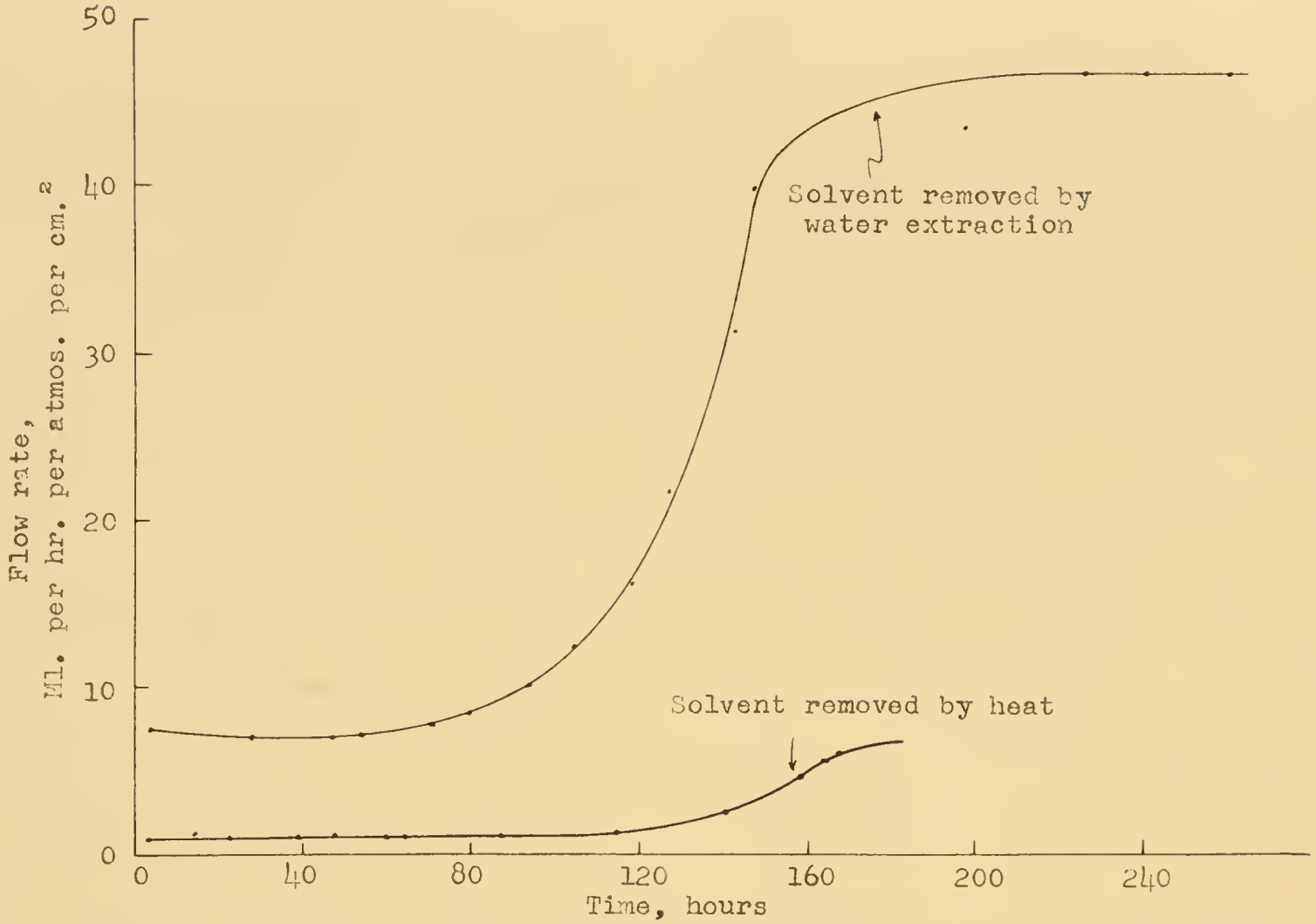

Fig. 17.--Effect of method of removing solvent on the variation of flow rate with time. Cellulose acetate containing 37.2% combined acetyl content was used.

is removed by water extraction, water has an opportunity to occupy a much greater proportion of the amorphous regions. Some of the decrease in flow rate caused by heating could be attributed to an increase in crystallinity; however, it is felt that obstruction of the amorphous regions is the primary cause for this loss in flow rate. Heating, as Mark has pointed out (35), causes irreversible packing which could block off some of the amorphous regions within the membrane.

Second, the water-cellulose structure apparently persists until long after the solute break-through has occurred. A break in the diffusion rate of water represents the beginning of extensive swelling of the structure. For the heat-treated membrane, the salt break-through occurred at 52 hours (Figure 15). Yet the break in diffusion rate of water for this same membrane occurred at 110 hours (Figure 17). The lag between solute and solvent break-through has been observed in varying degrees. It was more pronounced with heat-treated films.

Third, intermolecular forces stabilize water-cellulose structure. It is to be expected that the film prepared by removing the solvent through heating should be more resistant to failure since additional intermolecular forces between the polymers lying in the amorphous regions are set up. That this is a factor is indicated by the

longer life of this film. Note from Figure 17 that the heat-treated film lasted 100 hours before a break in the flow rate, as compared to fifty hours for the water-extracted film. Also, from Figure 15 it is seen that the stabilized film tended to maintain salt rejection for a little longer period of time. The two films reached 80 per cent salt rejection in approximately the same time. The film containing the greater amount of bound water, however, treated seven times as much water because the flow rate was seven times higher.

Fourth, film failure seems to be associated with a structural change rather than the development of cracks. From Figure 17 it is seen that after film failure, the rate of diffusion of water climbs up to a limiting value and levels off. This suggests that the completely failed film has a definite structure. If large breaks or cracks developed in the membrane, the flow rate would be expected to climb continuously with time. To investigate this point further, the semipermeability of completely failed films to fluorescein was checked. The fluorescein molecules were effectively blocked by the membrane indicating that the pores in the failed film were smaller than these molecules.

Reactions Between Solute and Membrane

Based upon the work that has been done on swelling agents for cellulose, it appears that swelling is a factor

in the failure of cellulose acetate to act as a semipermeable membrane. Neale (17) has developed a theory for the swelling of cellulose. He has shown that the hydroxyl groups of cellulose may be regarded as weak monobasic acids. These active hydrogens can then enter into exchange reactions with cations such as lithium and sodium. Accompanying the exchange reaction is a swelling effect.

When cellulose acetate undergoes swelling, the probability of hole formation increases so the diffusion rate of solute ions likewise increases. This relationship between swelling and hole-type diffusion of strong electrolytes is very important. Nicoll, Cox, and Conaway say in High Polymers (17) that swelling is absolutely necessary before alkali can penetrate into cellulose, and presumably this applies to other electrolytes.

Effect of acetylation.--The swelling of cellulose acetate depends upon the concentration of hydroxyl groups. As the degree of acetylation is increased, the number of active hydrogen atoms is reduced. Accordingly, membrane durability should be dependent upon the degree of acetylation.

In Figure 18 the durability of a film of 37 per cent acetyl content is compared to that of a film of 43 per cent acetyl content. Probably several factors contribute to the longer durability of cellulose triacetate (43 per cent

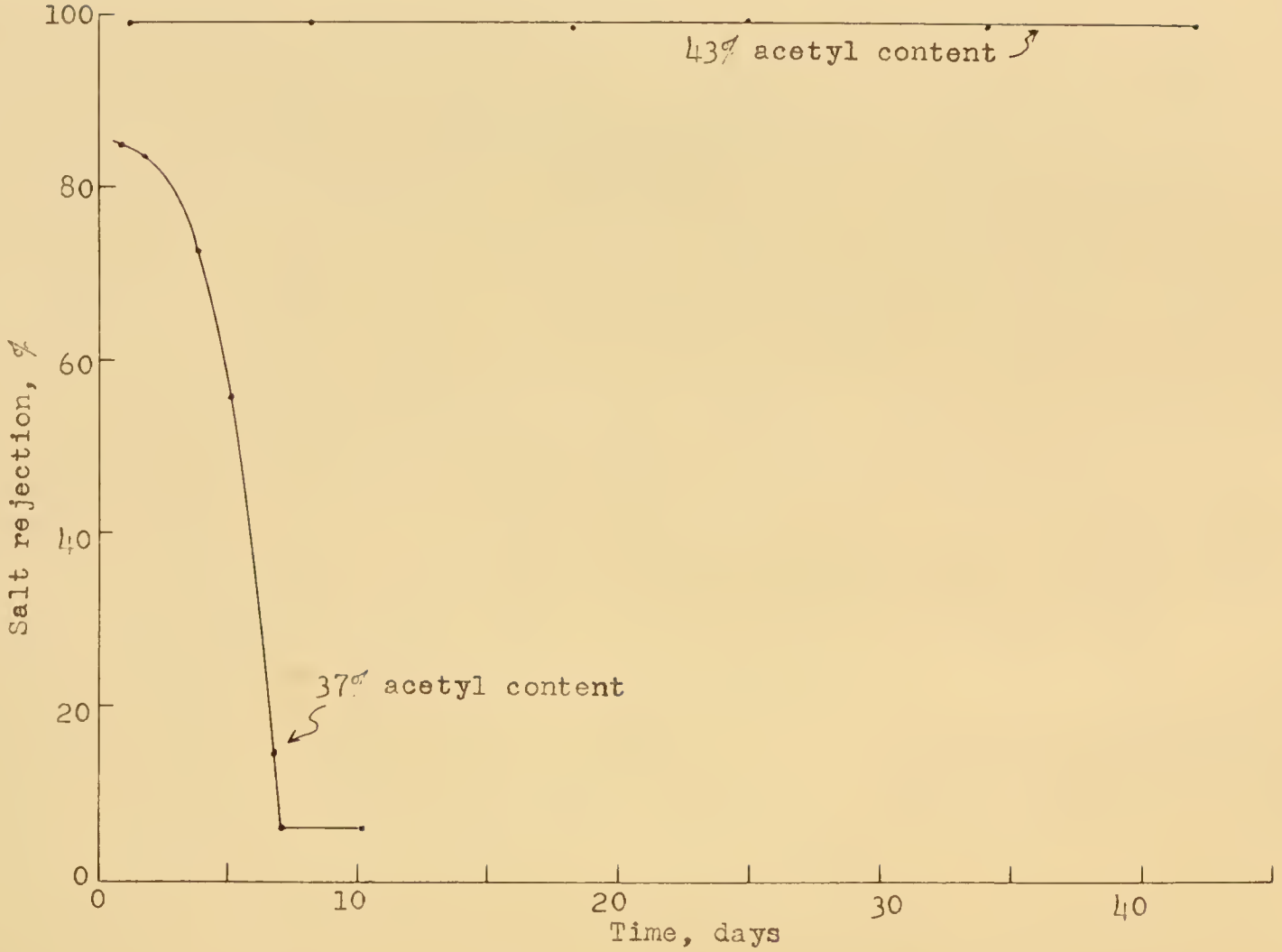

Fig. 18.--Effect of acetyl content on durability of cellulose acetate.

acetyl content). One would be that cellulose triacetate is more highly cross-linked by crystalline regions which would make it more resistant to swelling. Another reason is that the triacetate has fewer active hydrogens, so exchange (hence swelling) reactions with sodium ions would be limited, thereby permitting a longer period of semipermeability.

Effect of solute on durability.--If swelling is a factor in film failure, the life of the film should depend upon the type of solute in contact with it; i.e. solutes that have a high reactivity with the hydrogen should shorten film life. A series of tests was made to determine the effect of various solutes on the durability of the film. Again, films of 37 per cent combined acetyl content were used. The concentration of the solute in all runs was approximately 0.08 N.

In Figure 19 the durability of cellulose acetate in various solutions is illustrated. When dextrose was the solute, the film showed no signs of failure even after 300 hours of operation. When $MgCl_2$ was the solute, the film also lasted 300 hours with no appreciable drop in its semipermeability. Neither of these solutes would be expected to react with the acidic hydrogens in cellulose acetate. On the other hand, when NaCl was used as a solute, the film began to fail at 40 hours. Swelling, therefore, seems to be a factor in film failure, since the ions which cause

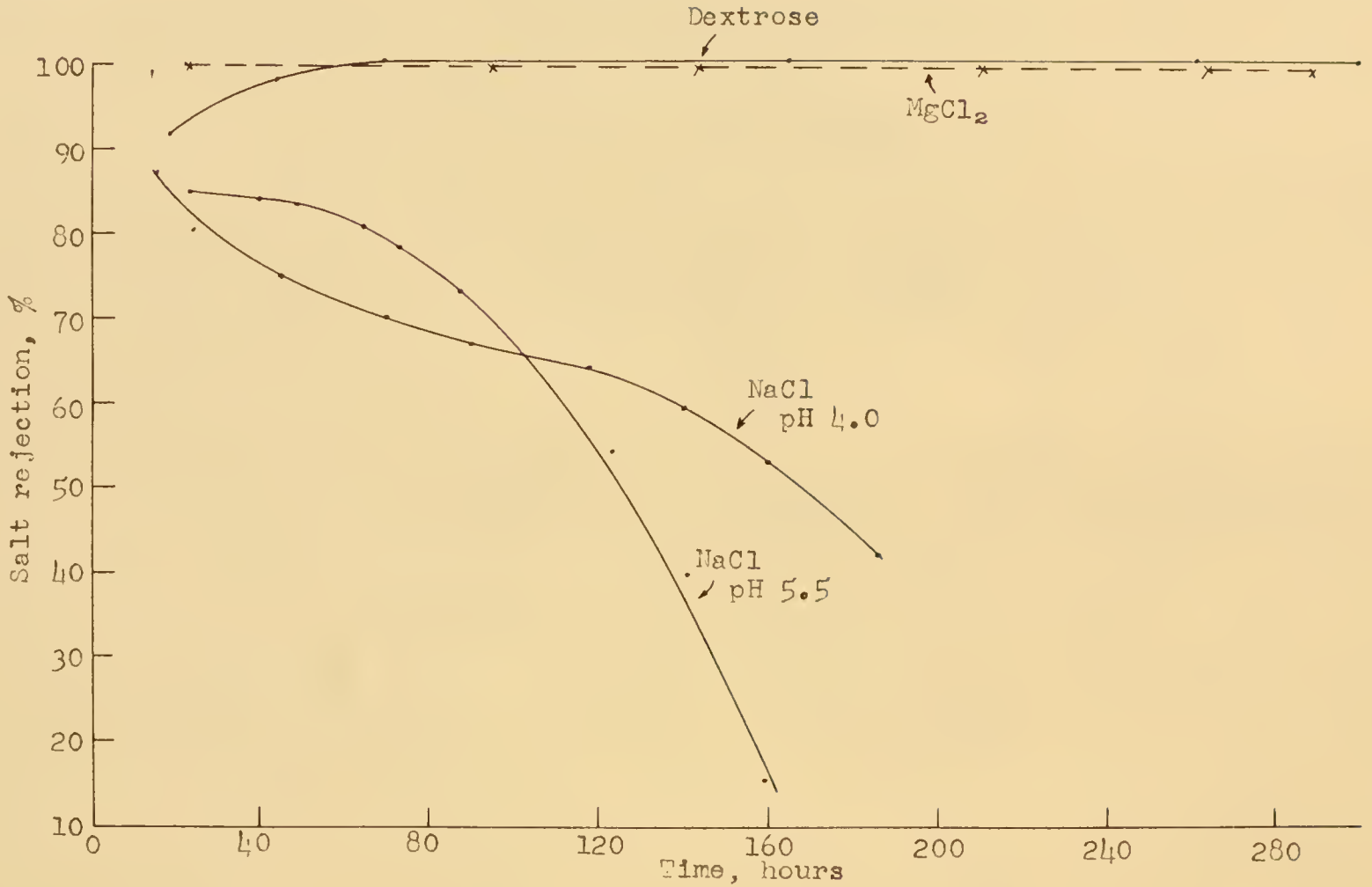

Fig. 19.--Effect of solute on durability of 37.2% cellulose acetate membranes.

rapid failure are swelling agents.

To obtain additional evidence to determine if the solute causes film failure, a run was made using pure water. After nine months of continual passage of water at 600 p.s.i., a membrane containing 37 per cent acetyl content exhibited no signs of failure. That is, there was no break or increase in the diffusion rate of water through the membrane.

If the reactivity of the acidic hydrogen atoms were reduced, then the life of the film should be extended. This can be done by lowering the pH. If the pH is lowered too far, however, the ester groups within the membrane may be hydrolyzed. As a compromise, a pH of 4 was selected. Hydrochloric acid was used to lower the pH. From the comparison of runs at high and low pH's included in Figure 19, it appears that the presence of hydrogen ions did retard the NaCl break-through. On the other hand, the rejection of chloride ions tended to level off at 60 per cent at the lower pH. This could be caused by the higher rate of diffusion of HCl.

A comparison of flow rates illustrates more clearly the effect of reducing the reactivity of the active hydrogen. Figure 20 gives a comparison of the flow rates through cellulose acetate at pH's of 4.0 and 5.5. The flow rate at the lower pH remained essentially constant up to 180 hours,

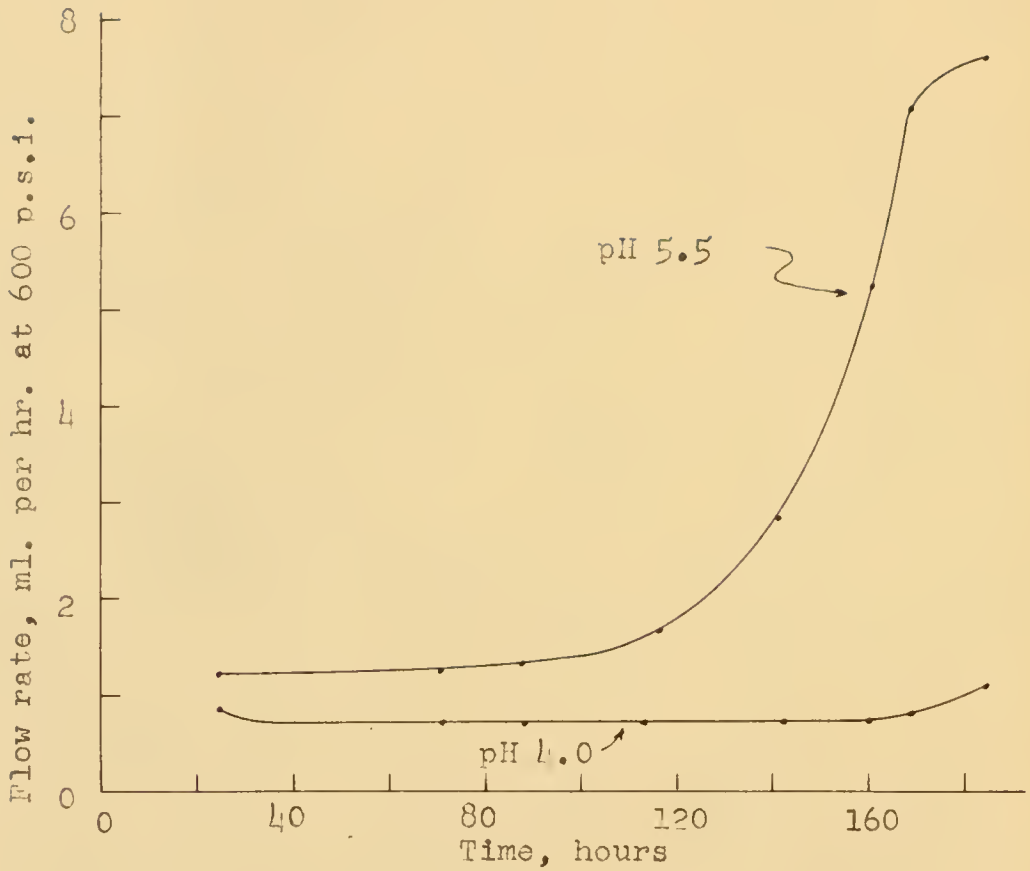

Fig. 20.--Effect of pH on durability of 37.2% cellulose acetate.

indicating no extensive change in the internal structures up to this time. Yet the NaCl solution at the higher pH caused a break in the flow rate after 87 hours. This difference, coupled with the fact that the flow rate at pH 4 was appreciably lower than at pH 5, indicates that the hydronium ions stabilized the bound water regions, possibly by reducing the reactivity of the active hydrogens in the membrane.

Mechanism of Membrane Failure

Although swelling is associated with membrane failure, hydrolysis is unquestionably responsible for extensive break-up of the water-cellulose acetate structure. Using infrared spectra, Kuppers (36) has shown that accompanying the decrease in semipermeability of cellulose acetate is an increase in the concentration of hydroxyl groups. The increase in hydroxyl groups is at the expense of carbonyl groups indicating that extensive hydrolysis is occurring.

The relationship between swelling and hydrolysis has not been established. It is assumed that swelling precedes hydrolysis. Initially, swelling results in the penetration of the solute into the membrane. The solute in turn causes hydrolysis. Since the product of the hydrolysis of cellulose acetate is more free hydroxyl groups,

Neale-type swelling continues. Concurrently, swelling and hydrolysis probably continue until the film is converted to cellulose.

The structure of the failed film must be different from other cellulose membranes since the diffusion rate of water through the failed films was very much lower. Furthermore, the failed films were mechanically weak and difficult to handle.

The lag between the solute break-through and the solvent break-through described earlier can possibly be explained as follows: Solutes such as NaCl penetrate cellulose acetate membranes by hole-type diffusion, whereas water diffuses by alignment. When swelling and hydrolysis commence, the probability of hole formation increases which increases the diffusion rate of NaCl. Yet the original structure is not altered enough to change the rate of diffusion of H_2O. As hydrolysis proceeds, the particular crystalline structure, which stabilizes the hydrogen-bound water structure, is continuously being altered. Even though the structure is continuously expanding, the bound water regions continue to fill up the pores within the membrane. A point is finally reached, however, at which water within the pores ceases to be extensively associated with the pore walls. Then the entropy of activation for diffusion of water is greatly reduced which causes the rate

of diffusion to increase.

Structural Changes

The structural arrangement of polymers has an important bearing on the semipermeability of cellulose acetate. Cellophane, it will be recalled, had a low degree of semipermeability because the internal structure was too open or expanded. It seemed of interest, therefore, to establish a correlation between the changes in internal structure of cellulose acetate and film failure. To do this work X-ray diffraction and optical studies were used.

X-ray studies.--X-ray diffraction spectra were made of two du Pont 88 CA-43 membranes. One had a salt rejection of 94.7 per cent and the other a salt rejection of 5.4 per cent. No bands appeared for the film that had 94.7 per cent salt rejection. A broad band appeared at approximately 4.4 Å for the failed film. This latter X-ray pattern was duplicated by using a failed film from an earlier experiment.

The band which appeared at 4.4 Å for the failed film ties in very well with the existing data and concepts. In connection with mercerization, a great deal of work has been done on lattice extension due to swelling. In High Polymers (17) the following concept is presented: Two types of swelling are possible--inter- and intra-micellular

swelling. Intra-micellular swelling is caused by sodium hydroxide, hydrazine, etc. attacking the crystalline regions of the polymer. Inter-micellular swelling is brought about by swelling between the micelles--the crystalline regions remaining unaffected. In the case of native cellulose, intramicellular swelling occurs in a direction normal to the 101 plane of the unit cell. The 101 planes are held together by hydrogen bonding. Looking down along the "b" axis with the cellulose chains coming out of the page, the unit cell of native cellulose is pictured in Figure 21. When a swelling agent enters the unit cell, the hydrogen bonds between the 101 planes are broken which causes an increase in the 101 spacings. As shown in Figure 22, increasing the 101 spacing flattens out the parallelogram. This flattening effect decreases the $10\bar{1}$ spacings to 4.4 Å. Depending upon the swelling agent, the 101 spacings may increase from 6 up to 16 Å. For NaOH it is 7.4 Å.

This mechanism for the swelling of native cellulose appears to apply to the swelling of cellulose acetate membranes. The band which appeared at 4.4 Å for the failed cellulose acetate corresponds to spacings between the $10\bar{1}$ planes in mercerized cellulose (Figure 22).

The fact that only the failed film diffracted the X-rays suggests that during failure the polymeric chains oriented into a plane parallel to the surface of the film.

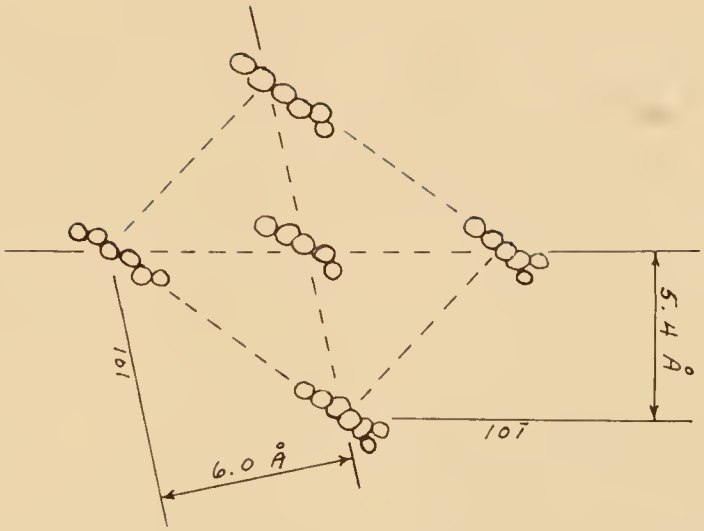

Fig. 21.--Unit Cell of Native Cellulose (17)

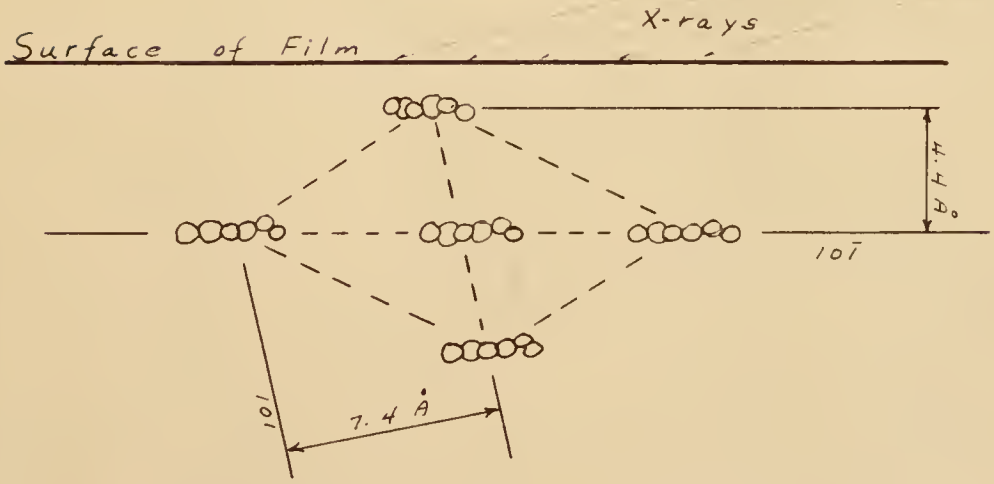

Fig. 22.--Unit Cell of Swelled Cellulose (17)

This rotated the $10\bar{1}$ planes into diffracting position. In Figure 22 the angle that the X-rays made with the surface of the film is inserted to show why only the $10\bar{1}$ plane caused diffraction.

Microscopic studies.--In order to study the effects of polymer orientation, the same two films used in the X-ray studies were also studied under the polarizing microscope. The polarizing microscope is extensively employed in the field of mineralogy for determining the degree of crystallinity of minerals. Drechsel (37), Spence (30), McNally (38), and others have employed the technique for studying the crystallinity of cellulose and its derivatives. The polarizing microscope permits one to obtain conveniently a quantitative index of the degree of crystallinity in a membrane and to determine the direction of orientation of the polymers.

When a beam of polarized light is passed through most crystalline substances, it will be broken into two parts--a fast ray and a slow ray. The difference in velocity between these two rays (which is called the birefringence) is governed by the degree of crystallinity in polymeric materials. The greater the degree of crystallinity, the greater the birefringence. The direction of vibration of the slow ray in cellulose acetate corresponds to the orientation of the polymer chains (37).

A Leitz Berek compensator was used with an American Optical polarizing microscope to measure the birefringence. Actually, the Berek compensator measures the retardation. That is, it measures the amount the slow ray is retarded behind the fast ray. This retardation produces interference colors which appear in the microscope. The higher the order of the color, the higher the retardation and, hence, the higher the crystallinity. The retardation is used to calculate the birefringence with the following formula (39):

$$n' - n'' = \frac{\Delta}{d}$$

$n' - n''$ = difference in refractive index between fast and slow rays called birefringence

Δ = retardation

d = thickness of sample in $m\mu$

First the birefringence was determined normal to the surface of the film. The results are recorded in Table 3.

These data indicate that both compression of the membrane and hydrolysis cause orientation of the polymers. Probably the number of unit cells was not increased, but rather those that were present were changed from a random orientation to an ordered arrangement.

The orientation in the film as received from the

TABLE 3

EFFECT OF SEMIPERMEABILITY ON BIREFRINGENCE

Film	Salt Rejection	Birefringence
88-CA-43 dry	As received (unused)	0.00019
88-CA-43 wet	94.7%	0.00046
88-CA-43 dry	94.7	0.00046
88-CA-43 wet	5.4	0.0022
88-CA-43 dry	5.4	0.0030

manufacturer was in the direction in which the film had been rolled.

An edge view of the film was obtained by cutting strips of the films 108 microns wide with two razor blades clamped together. By bending the strips, they could be made to stand on edge on the microscope stage. We were unable to measure the retardation with the Berek compensator because of interference from light which did not pass through the film. Attempts were made to block out the extraneous light, but none were successful. However, the retardation was estimated on the basis of the interference colors. Rogers (40) gives a color chart that is very useful for this purpose.

In Figures 23 and 24 the interference colors that appeared for the high semipermeability and low semipermeability cellulose acetate films are given. A magnification of

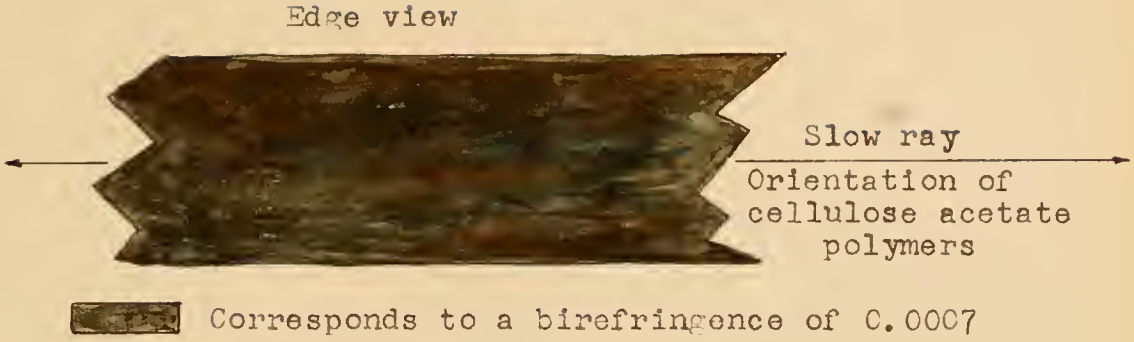

Fig. 23.--Birefringence of a du Pont CA-43 membrane that had a high salt rejection (over 90%).

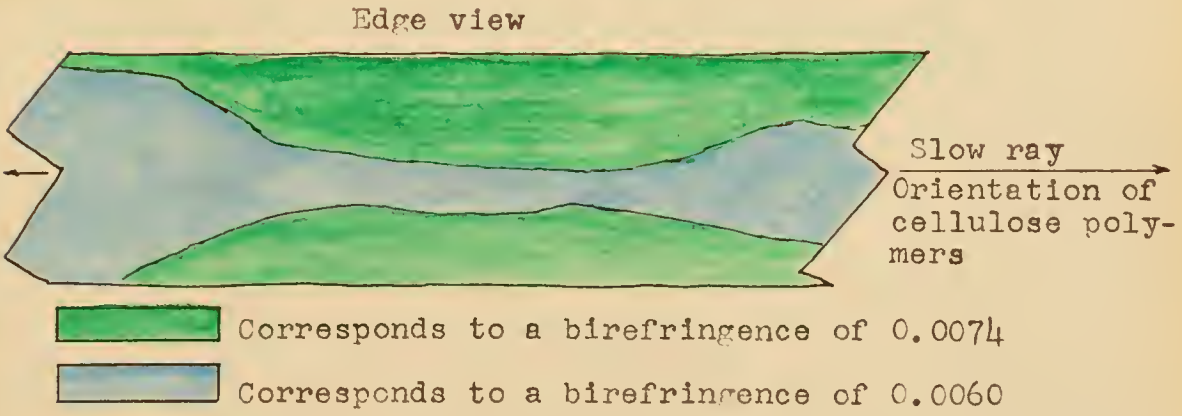

Fig. 24.--Birefringence of a du Pont CA-43 membrane that had failed (5.4% salt rejection).

X 860 was used. These observations indicate that film failure is associated with extensive orientation of the cellulose polymers into the plane of the membrane.

In view of previous work it is quite reasonable to expect this orientation. McNally (38) and Sissons (41) have shown that polymers will orient themselves to relieve stresses. In the case of cellulose acetate when the films begin to swell and hydrolyze, the chains become free to rotate. They then rotate into the plane of the film to relieve the stresses.

Based on the interference colors obtained from an edge view of a failed film, it appears that there is a slightly greater degree of orientation at the surfaces of the film than in the central regions. In the interior there may not be as much freedom of rotation. Apparently the orientation occurs at approximately the same rate throughout the film rather than starting on the salt water side and working its way through.

CHAPTER VI

RECOMMENDATIONS FOR AN IMPROVED MEMBRANE

In the last analysis, the use of semipermeable membranes for purifying sea water will depend upon the economics of the process. However, as a first step a semipermeable membrane with a very high flow rate will be needed. On the basis of the investigation described in this dissertation, it now is possible to propose some requirements for such a membrane.

According to this present study, the semipermeability of cellulose acetate is caused by regions of bound water within the membrane. The polymer network serves as a skeleton for setting up the bound water regions. These regions, it will be recalled, permit relatively rapid diffusion of water molecules while greatly retarding hole-type diffusion of sodium chloride. The problem, then, becomes one of designing a skeleton that will maintain a large amount of bound water.

To attain this objective, it appears that several factors in the design of the polymer network will need to be considered. First, the polymers that are used should

contain large numbers of sites for hydrogen bonding.

Second, sufficient cross-linking is needed to restrict the Brownian motion of the polymers that make up the network. It is postulated that the bound water regions can grow only when the kinetic energy of the polymers and water molecules are reduced enough to permit extensive association of the water with the polymer network. This being the case, the optimum degree of cross-linking would be related to the variables that affected the Brownian movement of the system. Pressure was found to restrict Brownian motion. Consequently less cross-linking would be needed at high pressures, say 3000 p.s.i., than at low pressures. Temperature is another variable that affects Brownian motion. Hence, if saline water is being purified at, say, 5°C., less cross-linking is required than at higher temperatures.

Third, the cells or channels within the polymer skeleton should be of optimum size for setting up bound water regions. The size is dependent upon how far a chain of hydrogen-bound water molecules can span without rupturing. At low temperatures--around the freezing point of water--hydrogen bonds are strong; so, relatively large cells can be used without increasing the probability of hole formation.

Fourth, the polymers should be cross-linked sufficiently to render them insoluble in water. In all

probability the membrane will be insolubilized when it is cross-linked enough to restrict Brownian motion.

Fifth, the polymer used for constructing the skeleton should be inert to chemical attack by sodium chloride or any other solute in the system.

Cellulose meets in part the requisites for a semipermeable membrane--it has sites for hydrogen bonding and sufficient cross-linking through crystallinity to set up bound water in its pores. However, only a small effective volume of the film is available for bound water. The rest is taken up with crystalline regions. It seems that the effective volume for bound water could be increased by employing cross-linking agents smaller than the crystalline regions of cellulose acetate.

Cellulose acetate has the further limitation of being subject to hydrolysis. Therefore, it is probable that ultimately some other type of semipermeable membrane will be developed for purifying saline water.

CHAPTER VII

SUMMARY

The primary objective of this investigation has been to explain why cellulose acetate behaves as a semi-permeable membrane in saline water. To explain this phenomenon, two different mechanisms for the transfer of water and ions through cellulose acetate membranes were formulated.

Those ions and molecules that cannot enter into hydrogen bonding with the membrane are transferred by hole-type diffusion. The rate of diffusion appears to be governed by a water-cellulose acetate structure. The reaction between water and the cellulose acetate polymers to form bound water regions is induced by compressing the membrane. As pressure is applied on the membrane, more bound water is produced which causes the rate of hole-type diffusion to decrease.

On the other hand, those ions and molecules that can associate with the membrane through hydrogen bonding actually combine with the membrane and are transported through it by alignment-type diffusion. The formation of the water-cellulose acetate structure does not appreciably diminish

the diffusion rate of water through the membrane.

Cellulose acetate begins to behave as an effective semipermeable membrane in saline water when it is compressed sufficiently to retard greatly the diffusion of NaCl.

Several types of experiments were conducted to support these hypotheses. The most important evidence was obtained from resistance experiments. The resistance of specific ions was measured across cellulose acetate at various pressures. It was observed that the rate of diffusion of those ions that cannot combine with the membrane actually does decrease as the membrane is compressed. The rate of diffusion of H_3O^+ that can enter into hydrogen bonding with cellulose acetate is much higher and is not appreciably reduced as the membrane is compressed. These resistance-pressure relationships are correlated with the semipermeability of the cellulose acetate.

On the basis of resistance-pressure relationships for cellophane, it appears that at sufficient pressures this membrane also should become semipermeable in strong electrolytes.

A secondary objective of this investigation has been to explain why cellulose acetate ceases to behave as a semipermeable membrane after a limited period of use. It was found that film failure is due to a chemical

reaction between the solute and cellulose acetate. X-ray diffraction and birefringence measurements were employed to show that extensive structural changes are brought about by this reaction between the solute and the membrane.

On the basis of this investigation it is considered that an improved semipermeable membrane can be obtained first, by using a polymer that is inert to chemical attack by sodium chloride, and, second, by increasing the amount of bound water regions within the membrane.

A P P E N D I X

Analytical Procedures

Preparation of Films

Determination of Dielectric Constants

Determination of Membrane Resistances

Analytical Procedures

Solute	Analytical Procedure
NaCl	Mohr titration for chloride ion
$MgCl_2$	Mohr titration for chloride ion
$CaCl_2$	Mohr titration for chloride ion
NaBr	Mohr titration for bromide ion
Ocean Water	Mohr titration for halides
NH_3	Titration with standard HCl
NaF	Conductivity
Na_2SO_4	Back titrated sulfate with barium chloride using a versenate indicator
H_3BO_3	Complexed H_3BO_3 with mannitol and made an acid base titration with KOH

During the early phase of this study, it was suggested that the reduction in chlorides was due to their adsorption rather than to the semipermeability of the membrane. To see if this were true the per cent salt rejections were calculated on the basis of conductivity measurements. For the most part the semipermeabilities calculated from conductivity measurements agreed with those calculated from chemical analysis.

Preparation of Films

Films were made by dissolving cellulose acetate in acetone and casting the solution on a suitable surface with

a doctor blade. The doctor blade could be rotated so that films of solution 6 or 8 mils thick could be spread. The solvent evaporated, leaving a film of cellulose acetate.

Several difficulties arose using this method. Because of the high humidity in the atmosphere, water would condense on the surface of the film during evaporation of the solvent. To avoid this difficulty the films were cast in a controlled atmosphere. This was accomplished by constructing a dry box which would permit the manipulation of the doctor blade by means of wires and also permit the casting of the cellulose acetate solution without admitting any outside air into the box. The removal of the solvent was controlled by passing a stream of dry air through the box. As a further precaution moisture was removed from the acetone with anhydrous sodium sulfate.

Since the films that were used were only 5 to 7 microns thick, the handling of them was a serious problem. Two methods were employed. A film could either be cast directly on cellophane or cast on glass and picked up by laying a sheet of wet cellophane on top of it. The cellophane then acted as a backing when the films were placed in the apparatus.

Above an acetyl content of 41 per cent, cellulose acetate becomes insoluble in acetone. Chloroform containing 5 per cent ethanol was used to dissolve cellulose

acetates with high acetyl contents.

Determination of Dielectric Constants

The dielectric constant of du Pont CA-43 was measured by placing the film between two brass plates approximately one inch in diameter and measuring the capacity with a heterodyne beat apparatus. The instrument that was used had an error of less than one $\mu\mu f$ (42). Pressure was applied to the film with a 10,000-pound hydraulic press. The brass plates were insulated from the press.

As pressure was applied to the film, changes in dielectric constant could have been due to four factors: (1) an increase caused by structural changes within the film, (2) a decrease caused by water squeezing out of the film, (3) an increase caused by better contact between condenser plates and the membrane, and (4) a change resulting from a change in the dielectric constant of water itself.

The change in dielectric constant due to structural and dimensional changes was corrected for by measuring the capacity of a dry film as a function of pressure. The $\Delta\epsilon$ versus p.s.i. curve for dry CA-43 also serves as a correction for any increase in dielectric constant due to better contact between the brass plates and the membrane. The change in dielectric constant for dry CA-43 is included in Figure 5.

To insure that the change in dielectric constant was not caused by a difference in water content, the film was first subjected to the pressure at which the capacitance was to be measured. After the squeezed-out water had been removed, the condenser formed by the brass plates and the film was wrapped with cellophane tape to prevent evaporation losses. Then the pressure was reduced to atmospheric pressure. The dielectric constant was determined at atmospheric pressure and the pressure was again increased for the determination at the desired pressure. The difference between the dielectric constant at atmospheric pressure and at the desired pressure was used for the ordinate in Figures 5 and 8.

The following expression from Weissberger (43) gives the relationship for calculating the dielectric constant from the capacitance:

$$\epsilon = \frac{d}{0.0885\ A}\ C$$

ϵ = dielectric constant

C = capacitance in micromicrofarads

d = distance between plates in centimeters

A = area of plates in square centimeters

The dielectric constant determinations were made at a frequency of 250 KC.

It is felt that the procedure employed gave the necessary accuracy. The dielectric constant of the dried sample of du Pont cellulose acetate was found to be 3.1 to 3.4 which lies within the range of dielectric constants listed in Modern Plastics for cellulose acetate (44). Besides, the change in dielectric constant was needed instead of the actual value.

Determination of Membrane Resistances

A drawing of the cell used for measuring resistances is shown in Figure 25. The circular carborundum whetstones serve two purposes. First, they compress the film uniformly and second, they act as electrolyte chambers. When saturated they hold between 4 and 5 ml of solution apiece. With this apparatus, compressive stresses of over 8000 p.s.i. can be applied to a film. To eliminate evaporation losses, the sides of the carborundum stones were covered with wide elastic bands and wrapped with "Presstite" Insulation Tape. This tape, which is pliable like putty, was pressed to cover all cracks.

Figure 26 is a schematic of the electrical circuit used for measuring the resistance across the cell. As indicated in the figure, the voltage drop across the cell was measured directly. The current was determined by measuring the voltage drop across a known resistance and using Ohm's law. The double pole, double throw switch was used for

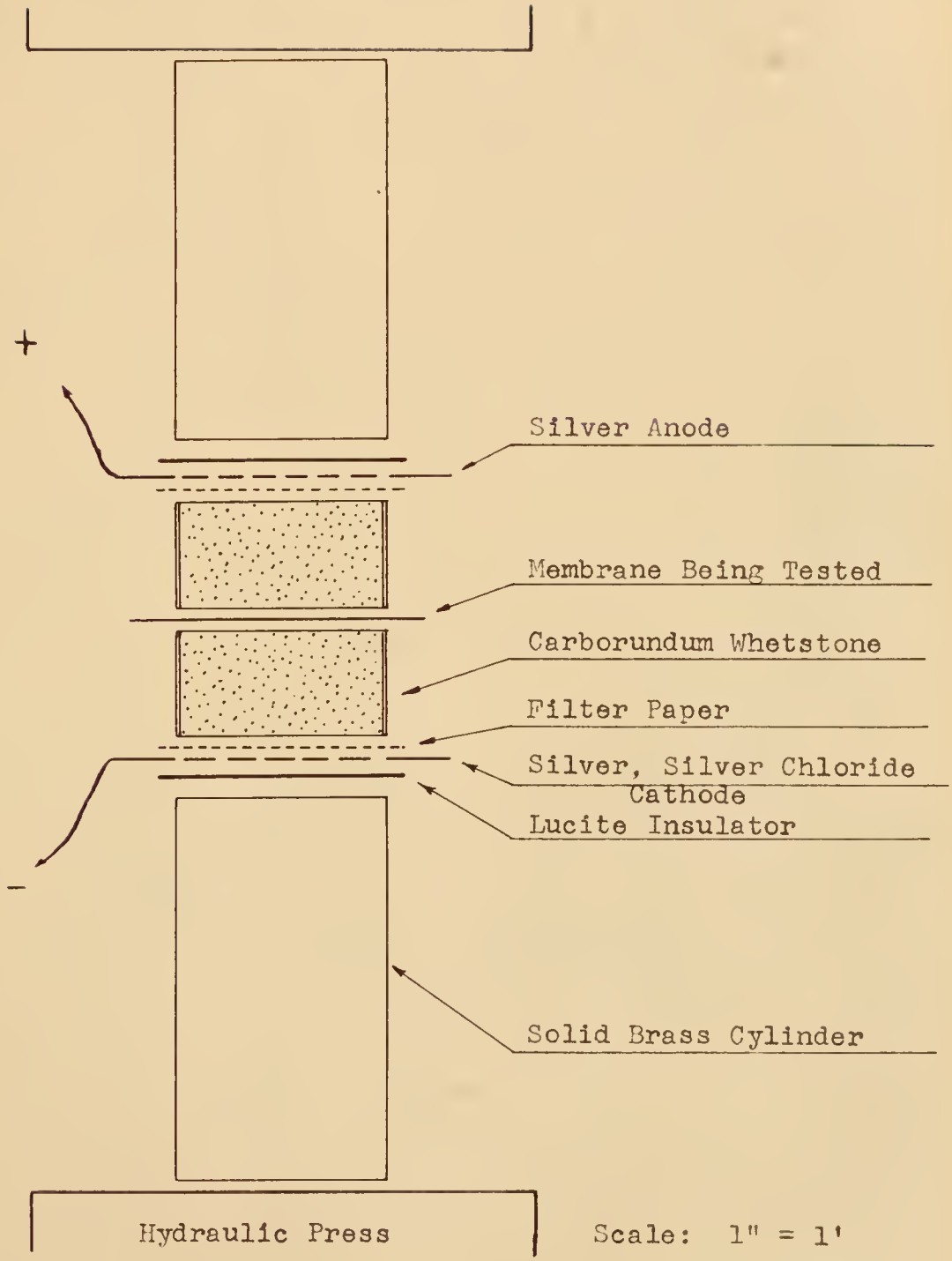

Fig. 25.--Apparatus for measuring membrane resistances.

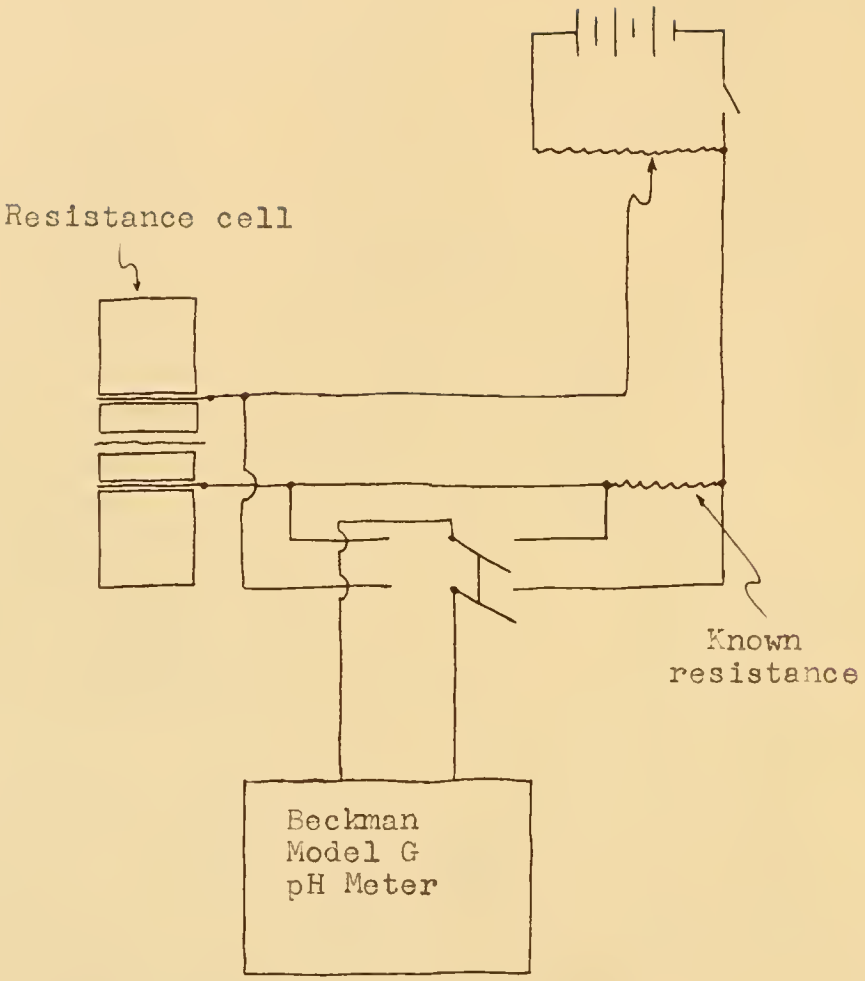

Fig. 26.--Wiring diagram for determining membrane resistances.

applying the potential drop across either the known resistance or across the cell to the Beckman Model G pH meter. The voltage was determined within an accuracy of $\pm$ 0.1 millivolt.

In the selection of electrodes, two factors were considered. First, the products of the electrode reactions had to be non-gaseous. Second, the products of the electrode reactions should not introduce interfering ions into the system.

To measure the membrane resistance of chloride ions, discs of Amberplex anion permeable membranes in the chloride form were placed on both sides of the cellulose membrane. The cell was compressed to the maximum pressure at which resistances were to be measured, and the excess solution that squeezed out was removed. After wrapping the cell with "Presstite" tape, resistance measurements were made as the pressure was reduced. Two to three minutes were allowed at each pressure before measuring the resistance. A weighted lever was used to apply pressures up to 1600 p.s.i. For pressures up to 8000 p.s.i., a hydraulic press was used.

The same procedure was employed for measuring the membrane resistance of Na^+. However, an Amberplex cation permeable membrane in the sodium form was used on each side of the cellulose membrane. The membrane resistance of H_3O^+

was determined by using the cation permeable membrane in the acid form.

To measure the membrane resistance of NaCl, no ion exchange membranes were used.

The carborundum blocks were saturated with a 0.018 N NaCl solution for the Cl^-, Na^+, and NaCl determinations. The blocks were saturated with 0.018 N HCl for the H_3O^+ resistance determinations.

The membrane resistance was obtained from the following expressions:

$$\text{Membrane resistance} = \left(\begin{matrix}\text{Total cell}\\ \text{resistance}\end{matrix}\right) - \left(\begin{matrix}\text{Resistance of cell without}\\ \text{the cellulose membrane}\end{matrix}\right)$$

$$\text{Cell resistance} = \frac{\text{Voltage across cell}}{\text{Current passing through the cell}}$$

$$\begin{matrix}\text{Current passing}\\ \text{through the cell}\end{matrix} = \frac{\text{Voltage across known resistance}}{\text{Known resistance}}$$

The units of membrane resistance are ohms for the total film area (7.1 square centimeters).

The resistance across the ion exchange membranes is very low and does not vary significantly with pressure.

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BIOGRAPHICAL ITEMS

Ernest J. Breton was born in Chuquicamata, Chile, South America, on February 5, 1924. His father's work as a mining engineer took the family to many parts of the United States and Canada. In 1942 he entered the Alabama Polytechnic Institute, Auburn. Shortly after enrolling, he was called to active duty with the Army Air Corps. He was commissioned as a communications officer and spent eighteen months in the Pacific theater.

After being released from active duty in 1946 he entered the University of Missouri School of Mines and Metallurgy, Rolla, and obtained bachelor of science and master of science degrees in 1950. Several months' employment with the Rohm and Haas Company, Philadelphia, followed. Soon after finishing school he was recalled to active duty with the Air Force during the Korean War. He served eighteen months with the Air Research and Development Command at Wright-Patterson Air Force Base, Dayton, Ohio.

In 1953 he enrolled in the graduate school of the University of Florida, Gainesville, to pursue a doctor's degree in physical chemistry with a minor in physics. For the past three and a half years he has held a research

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

January 26, 1957

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